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CATALYTIC ISOMERIZATION OF δ-OXIDES (TETRAHYDROPYRANS) TO ALIPHATIC CARBONYL COMPOUNDS

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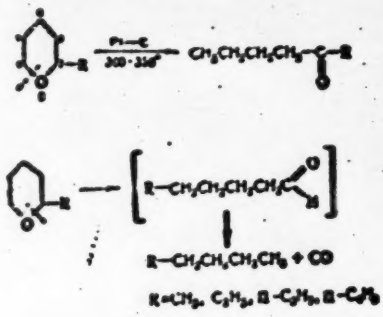
Until recently, it has been assumed that γ- and δ-oxides, in contrast to α-oxides, cannot undergo isomerization with ring cleavage to aliphatic carbonyl compounds. However, we found that γ-oxides (tetrahydrofuran and its homologs) undergo isomerization in the vapor phase at 250° over platinized carbon, the ring opening to yield chiefly aliphatic ketones [1]. The small amount (~5-10%) of aldehydes obtained during the reaction readily undergo decarbonylation with the formation of alkanes under these conditions.

It might be expected that δ-oxides (tetrahydropyrans) would isomerize to open-chain carbonyl compounds under the conditions under which isomerization of γ-oxides takes place. As a matter of fact, we have found that tetrahydropyrans having an alkyl substituent in the α-position do undergo vapor-phase isomerization over platinized carbon at 300-350°, the ring opening to yield the corresponding aliphatic ketones and also some alkanes:



In all cases, ketones were obtained in yields of 70-80%, and the yields of hydrocarbons did not exceed 20-30%. This shows that the predominant course of the isomerization of α-alkyltetrahydropyrans is, as in the case of γ-oxides, opening of the ring at the C—O bond furthest removed from the alkyl side chain (the 1,6-bond). The isomerization of α-alkyltetrahydropyrans proceeds just as smoothly as the isomerization of γ-oxides; the reaction products consist only of ketones and aliphatic hydrocarbons. As regards the ease of cleavage of the tetrahydropyran ring, here again there is an analogy to the γ-oxides. Since the isomerization of δ-oxides was carried out at a higher temperature, the degree of conversion to aliphatic ketones and aldehydes was higher than the degree of conversion of the corresponding γ-oxides and comprised 50-60% per pass.

EXPERIMENTAL PART

The α-methyl-, α-ethyl-, α-n-propyl-, and α-n-butyltetrahydropyrans were synthesized by the method of Paul [2]; they had the following properties:

1) α-Methyltetrahydropyran, b.p. 101-102° (750 mm), d_4^{20} 0.8570; n_D^{20} 1.4187.

2) α-Ethyltetrahydropyran, b.p. 128-129° (752 mm), d_4^{20} 0.8566; n_D^{20} 1.4248.

3) α-n-Propyltetrahydropyran, b.p. 152-153° (754 mm), d_4^{20} 0.8552; n_D^{20} 1.4290.

4) α-n-Butyltetrahydropyran, b.p. 176-177° (750 mm), d_4^{20} 0.8570; n_D^{20} 1.4350.

The catalyst was platinized carbon containing 10% platinum; it was prepared by impregnation of activated carbon with chloroplatinic acid solution and subsequent treatment with formalin and 50% KOH. Before each experiment, hydrogen was passed for 2-3 hours over the catalyst at reaction temperature. The α-alkyltetrahydropyran, either in a stream of hydrogen or alone, was fed to the catalyst at a space rate of 0.1 hours^{-1}. The liquid product was dried with $CaCl_2$ and distilled in an efficient column. The physical properties of the ketones formed during the isomerization of α-methyl-, α-ethyl-, α-n-propyl-, and α-n-butyltetrahydropyrans and the melting points of their semicarbazones are presented below.

1) 2-Hexanone, b.p. 126-126.5°; d_4^{20} 0.8115; n_D^{20} 1.4018; semicarbazone m.p. 120-121°.

2) 3-Heptanone, b.p. 147-147.2°; d_4^{20} 0.8192; n_D^{20} 1.4095; semicarbazone m.p. 101°.

3) 4-Octanone, b.p. 166.5°; d_4^{20} 0.8190; n_D^{20} 1.4135; semicarbazone m.p. 96°.

4) 5-Nonanone, b.p. 186-187°; d_4^{20} 0.8270; n_D^{20} 1.4200; semicarbazone m.p. 89°.

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SYNTHESIS OF HIGHER KETONES BY LIQUID-PHASE OXIDATION OF SECONDARY ALCOHOLS

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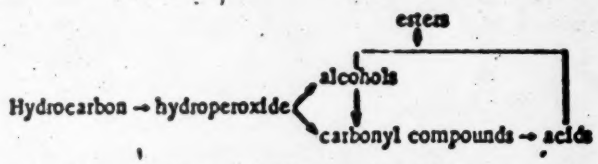
As a result of the work which has been carried out up to the present time on the mechanism of the liquid-phase oxidation of paraffinic hydrocarbons, it has become apparent that this is a stepwise process. The succession of the individual stages involved in the oxidative conversion of paraffinic hydrocarbons can be represented by the following scheme [1-3].



The experimental data available in the literature show [4] that, as a rule, a considerable amount of carbonyl compounds is formed during the process of producing synthetic fatty acids by oxidation of solid paraffins. In addition to secondary alcohols, a certain amount of ketones is always present in the products of the oxidation of higher paraffinic hydrocarbons in the presence of boric oxide [5].

The formation of carbonyl compounds (see scheme) can take place, first, as the result of the decomposition of the hydroperoxides [6] and, second, by oxidation of the alcohols present in the reaction zone.

It was of interest to obtain experimental data on the possibility of the occurrence of oxidation of alcohols under conditions analogous to those used for the liquid-phase oxidation of hydrocarbons, and it was also of interest to establish the possible existence of directed oxidation of secondary alcohols to ketones.

In carrying out the present investigation, we used higher aliphatic alcohols obtained from a pilot plant operation of the process developed in the Academy of Sciences SSSR [5]. The content of secondary alcohols in this product was about 90 mole % [7]. The alcohol fraction boiling in the range 125-170° at 1 mm Hg (C_{18}-C_{19}) was used in the oxidation; this fraction had a hydroxyl number of 220.0, a carbonyl of 20.0, and acid number 1.1, an ester number of 3.4, d_4^{20} 0.8486, n_D^{20} 1.4496, and a freezing point of +8.6°.

The liquid-phase oxidation of higher alcohols was carried out in an apparatus and by a method described by us previously [5]. 65 g of these alcohols was used in each oxidation experiment; the specific consumption of oxidizing gas was 1000 liters/kg-hour (when oxygen was used, the specific consumption was 200 liters/kg-hour). The effect of the reaction conditions (temperature, concentration of oxygen in the oxidizing gas, and oxidation time) on the oxidation of these higher alcohols was investigated, as was the effect of certain promoters on the composition of the products ("oxidate").

The effect of temperature on the oxidation of higher alcohols was studied in the range 120-180° using a nitrogen-oxygen mixture containing 6.0-6.5 wt. % oxygen and an oxidation time of 4 hours (Table 1).

TABLE 1

The Effect of Oxidation Temperature on the Degree of Conversion and on the Product Composition in the Oxidation of Higher Alcohols

Oxidation temp., deg C	Oxidate analysis			Amt. of oxygen-containing cmpds. formed (ketones and acids)		
	Acid No.	Ester No.	Carbonyl No.	Total, mmole per g	Mole %	
					acids	ketones
120	1,0	0,0	20,2	—	—	—
140	5,5	13,1	51,0	0,89	36,4	63,6
165	22,0	34,5	112,0	2,05	44,4	55,6
180*	30,0	47,0	115,0	3,07	44,7	55,3

* Oxidation time, 3.5 hours.

TABLE 2

The Effect of the Concentration of Oxygen in the Oxidizing Gas on the Degree of Conversion and on the Product Composition in the Oxidation of Higher Alcohols

Concn. of oxygen in oxidizing gas (vol. %)	Oxidate analysis			Amt. of oxygen-containing cmpds. formed (ketones and acids)		
	Acid No.	Ester No.	Carbonyl No.	Total mmole/g	Mole %	
					acids	ketones
Oxidation temperature, 140°						
3,7	2,8	0,0	42,0	0,66	11,0	89,0
6,0	5,5	13,1	51,0	0,89	36,4	63,6
21,0	28,2	33,7	104,0	2,78	46,0	54,0
100,0	94,0	46,0	150,0	4,82	51,8	48,2
Oxidation temperature, 165°						
3,7	11,3	19,7	66,0	1,37	39,4	60,6
6,5	23,1	38,9	110,0	2,71	40,7	59,3
21,0	113,0	63,1	120,0	5,11	61,6	38,4

As may be seen from the experimental data, reaction temperature is a factor having a considerable effect on the conversion of the original alcohols and on the composition of the resulting oxidation products. With an increase in reaction temperature, there is an increase in the acid fraction of the reaction products and a decrease in the ketone fraction. The ketone fraction decreased from 63.6 to 55.3 mole % with an increase in the temperature from 140 to 165°. There was a simultaneous increase in the degree of conversion of the original alcohols. Similar effects were found during the study of the oxidation of alcohols with a nitrogen–oxygen mixture containing 3.7% oxygen and also with air and with oxygen. It should be noted that the oxidation of alcohols proceeds at a low rate at a temperature of 120°. During oxidation with a nitrogen oxygen mixture containing 6.0 % oxygen, the degree of conversion did not exceed 1.5–2.0 mole % over an 8-hour period; when the oxidation was carried out for 4 hours with oxygen, the degree of conversion was 12.0–15.0 mole %.

Carrying out the oxidation of alcohols at higher temperatures (particularly with a high concentration of oxygen in the oxidizing gas) makes it impossible for a significant amount of carbonyl compounds to accumulate in the oxidate, apparently owing to rapid oxidation of the carbonyl compounds to acids. Under these conditions, the major product of the oxidation of alcohols is acids (free and combined as esters).

A study of the oxygen concentration in the oxidizing gas, which was carried out at 140° (oxidation time, 4 hours) and at 165° (3 hours), showed that an increase in the oxygen concentration in the reaction zone increases the degree of conversion of the original alcohols and decreases the relative yield of ketones—the ketone portion in the oxidation products of the alcohols (Table 2).

As a rule, the rate of the oxidation reaction depended to a great extent on the concentration of oxygen in the oxidizing gas. The lower the concentration of oxygen in the oxidizing gas, the greater was the relative yield of ketones [particularly at low temperatures (120–140°)]. Oxidation with a gas mixture with a high oxygen content for the purpose of obtaining ketones is unwise, since a large amount of acids is formed in this case.

Investigation of the products of the oxidation of alcohols at various reaction times (temperature of 140°, oxidation with air) showed that an increase in the oxidation time changes not only the degree of conversion of the original alcohols, but also changes the composition of the products obtained (Table 3, Figure 1).

An increase in the oxidation time led to an increase in the degree of conversion of the original alcohols and to a decrease in the relative yield of ketones with an increase in the yield of acids and esters. The amount of ketones in the reaction products decreased from 88 to 45 mole %.

The experimental data obtained permitted us to select conditions for the oxidation of alcohols providing for yields of ketones of up to 60 mole %, based on the alcohols converted, and of a degree of conversion of the original alcohols of 40–45 mole %. These oxidation conditions are as follows: temperature, 165°; oxygen content of the oxidizing gas mixture, 6.0–6.5 %; specific consumption of the oxidizing gas, 1000 liters/kg/hour; and oxidation time, 3 hours. A higher yield of ketones can be obtained at a lower degree of conversion of the original alcohols.

TABLE 3

The Effect of Oxidation Time on the Degree of Conversion and on the Product Composition in the Oxidation of Higher Alcohols

Oxidation time, hr	Oxidate analysis			Amt. of oxygen-containing cmpds. formed (ketones and acids)		
	Acid No.	Ester No.	Carbonyl No.	Total, mmole/g	Mole %	
					acids	ketones
1	0.6	9.0	78.8	0.19	11.5	88.5
2	12.0	1.9	84.3	0.26	29.0	71.0
4	25.1	27.1	102.0	2.22	36.8	63.2
5	28.2	23.2	104.6	2.59	46.0	54.0
6	29.0	41.2	128.0	2.85	45.0	54.0

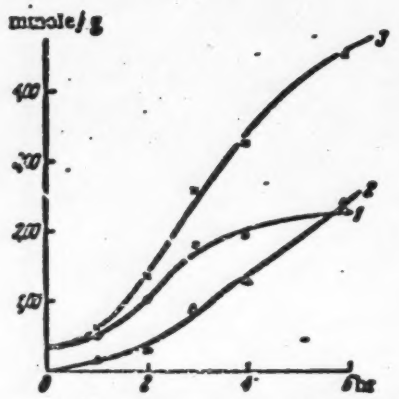


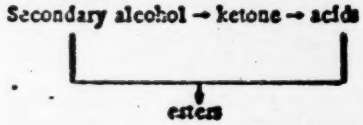
Fig. 1. Kinetics of the accumulation of oxygen-containing compounds (temp. 140°; oxidation with air). 1) Carbonyl compounds; 2) acids (free and combined); 3) total content of oxygen-containing compounds.

A study of the oxidation of alcohols in the presence of various promoters (salts of metals of variable valence) showed that their effect on the oxidation of alcohols is of a nature similar to their effect on the oxidation of hydrocarbons. For example, the introduction of manganese salts into the reaction zone led to a significant increase in the yield of acids. The promoters studied (Co, Ni, Mn, Fe, Cr, Cu, and Sn salts) had an effect on the rate of oxidation of the alcohols. However, not one of them had a selective effect on the oxidation of alcohols to ketones.

The introduction of iron pentacarbonyl into the reaction zone led to a sharp inhibition of the oxidation process, which indicates that this reaction is a radical type.

Under the conditions studied, secondary alcohols are oxidized to ketones at a significant rate. This constitutes experimental confirmation of the idea that the secondary alcohols formed during liquid-phase oxidation of hydrocarbons can undergo further oxidative conversion, yielding ketones which, in turn, can undergo oxidation to acids. These data are in good agreement with the results of an investigation of the effect of boric acid and of boric oxide on the liquid-phase oxidation of paraffinic hydrocarbons [8].

The presence of esters in the products of the oxidation of alcohols indicates that it is possible for the original alcohols to undergo esterification by the acids formed in the course of the oxidation. The cycle indicated above for the oxidative conversion of secondary alcohols can be represented by the schemes



The curve showing the accumulation of carbonyl compounds in the oxidation products (Figure 1) shows that when a certain concentration of ketones is reached in the reaction zone, further accumulation of ketones does not occur. In this case, there is apparently established in the reaction zone a dynamic equilibrium in which the rate of further conversion of ketones becomes equal to the rate of formation of ketones.

With the aim of separating the carbonyl compounds formed during the oxidation of the secondary alcohols, the oxidate was subjected to saponification with an 0.5 N aqueous solution of a base. The solution of fatty acid salts was separated from the oil layer and extracted with ether. After distillation of the ether, the resulting product, which consisted of a mixture of carbonyl compounds and alcohols, was separated by the borate method. The alcohols contained in the above product were esterified with boric acid; the resulting borate esters of the alcohols were separated from the carbonyl compounds by distilling the latter under vacuum. The distillate, which consisted of a mixture of ketones (a reaction for aldehydes with fuchsin-sulfurous acid was negative), was a lemon-yellow liquid characterized by the following properties: carbonyl number, 200.0; acid and hydroxyl numbers, 0; ester number, 4.2; d_4^{20} 0.8420; n_D^{20} 1.4441; f.p. + 10.6°

To sum up, the work showed that higher ketones can be obtained by liquid-phase oxidation of secondary alcohols. The conditions found for the directed oxidation of higher secondary alcohols to ketones provided for a

ketone yield of about 60 mole% based on the converted alcohols (at a degree of conversion of 40–45 mole%).

Higher ketones can also be obtained by dehydrogenation of secondary alcohols over appropriate catalysts. Experimental data on this question will be published by us in the near future.

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THE MECHANISM OF CATIONIC POLYMERIZATION UNDER THE INFLUENCE OF METAL HALIDES

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The cationic polymerization of olefins by metal halides has been interpreted in two ways. The first theory, proposed by Hunter and Yohe [1], ascribed the catalysis to the formation of a polarized complex between the metal halide and the olefin:

$$PX_n + \overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}} \rightarrow PX_n^- - \overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}^+,$$

and supposed that the carbonium ion thus formed started the chain reaction.

Subsequently it was found that in solvents of low dielectric constant (hydrocarbons and carbon tetrachloride) neither polymerizations [2] nor alkylations [3] nor isomerizations [4] could be effected by a metal halide alone, but that a third substance, called the cocatalyst, is required. The most common, and indeed ubiquitous co-catalyst is water; other substances proved to act in this capacity are alcohols [5], organic acids [5,6] and nitro-compounds [7]. In each case the catalysis can be ascribed to a complex protonic acid $PX_nA^-H^+$:

$$PX_n + AH \rightarrow PX_nA^-H^+,$$

$$PX_nA^-H^+ + M \rightarrow PX_nA^-HM^+.$$

A carbonium ion is formed by proton-transfer from the complex acid to the olefin. The polymerization is initiated by the carbonium ion, and the growing end of the polymer consists of an ion pair. For reactions in alkyl halide solvents the situation was less clear. Early experiments [8] suggested that the addition of water had little or no effect. This prompted Pepper to suggest [8] that the alkyl halide solvent itself was acting as cocatalyst:

$$PX_n + RX \rightarrow R^+PX_{n+1}^-$$
$$R^+PX_{n+1}^- + M \rightarrow RM^+PX_{n+1}^-$$

Experiments by one of us [9] appeared to confirm this for certain alkyl halides, but also showed that, at any rate in the system styrene - $TiCl_4$ - $(CH_2Cl)_2$, the addition of water accelerated the reactions. Further, and much more cogent evidence for the cocatalytic effect of some alkyl halides was produced by Colchlough and Dainton [10]. They showed that for the system styrene - $SnCl_4$ both $(CH_2Cl)_2$ and t-C_4H_9Cl acted as cocatalysts, but only in solvents of dielectric constant greater than about 7.

Before the publication of Colchlough and Dainton's work, Gantmakher and Medvedev [11] had revived Hunter and Yohe's theory of direct initiation, but restricted it to solvents of moderately high dielectric constant. They maintained that in such solvents neither a protonic nor an alkyl halide cocatalyst is required. The experiments of Colchlough and Dainton make this appear unlikely, although they do not disprove it completely. It is important to realize that several types of initiation could coexist in the same system; even if in certain systems cocatalysis

TABLE 1

Temp. C	Concentration of $TiCl_4$ mol/L	Isobutene concen. mol/L	Yield %	Styrene concen. mol/L	Yield %	% Yield on addition of water
—14,3	0,00220	0,0893	6,4	0,0685	8 5	55,0
—29,1	0,00225	0,0912	15,5	0,0560	15,1	69,4

Notes. (1) The % yield is calculated with respect to the total number of gram-molecules of both monomers added. (2) The intervals between the start of the isobutene polymerization and the addition of the styrene were about 3 minutes, those between the addition of styrene and the addition of water about 5 minutes.

by alkyl halides was proved, this does not exclude the existence of a concurrent direct initiation by the Hunter-Yohe, Gantmakher-Medvedev mechanism.

However, our own experiments now provide unambiguous proof that Gantmakher and Medvedev's modification of Hunter and Yohe's theory is not applicable to the system CH_2Cl_2-$TiCl_4$ - H_2O with styrene or isobutene. We have developed an apparatus [12] in which the amount of residual water per reaction mixture (100 ml.) can be reduced to less than 10^{-5} moles. With CH_2Cl_2 as solvent and $TiCl_4$ as catalyst, we found that isobutene polymerizes to an extent which is strictly proportional to the amount of water present— up to a certain limiting water concentration giving 100% yield. The yield at a given water concentration increases with decreasing temperature. A polymerization which has stopped for lack of water can be restarted by the addition of more water, but not by the addition of more $TiCl_4$. For styrene, the behavior pattern is quite different: However low the concentration of water may be, the reaction always goes to 100% yield.

Thus, our experiments with isobutene show that for this monomer the Gantmakher and Medvedev theory is not applicable; they also show that for isobutene CH_2Cl_2 is not a cocatalyst to $TiCl_4$. However, it was still possible that the polymerization of styrene at the lowest water concentration was due not to residual water, but either to cocatalysis by the solvent or to direct initiation by the Gantmakher and Medvedev mechanism. However, since we found the M wt. to be independent of both the water and the $TiCl_4$ concentration and the rate at low water concentration to be independent of the $TiCl_4$ concentration, these alternatives appeared unlikely.

We settled the matter finally in the following way.

In a series of experiments under conditions of extreme dryness isobutene was polymerized by $TiCl_4$. Only a small fraction of the isobutene polymerized, consuming the residual water, and the reaction then stopped. Dry styrene was then added. A further slight reaction occurred which stopped after a few seconds. This was presumably caused by a trace of water in the styrene. When it was quite certain that the polymerization had ceased, enough water was added to the system to give 100 % polymerization. There ensued a fast polymerization at the end of which a 100 % yield of a copolymer of styrene and isobutene was obtained. Some typical results are shown in the Table. They prove conclusively that in the solvent CH_2Cl_2 neither isobutene nor styrene can be polymerized by $TiCl_4$ alone, and that therefore in this system, at any rate, there is neither cocatalysis by the solvent nor direct initiation by the $TiCl_4$ alone, as was postulated by Gantmakher and Medvedev.

The kinetic arguments which these authors adduce to support their theory are not decisive— they are based on the "steady state" hypothesis which is by no means always valid for cationic polymerizations. There is no independent evidence for the various types of initiation which they give, and they are too general to be useful. Without going into a detailed discussion we would merely point out that under identical conditions (CH_2Cl_2 - -$TiCl_4$-H_2O, temp. -30° to -95°) the initial rate of polymerization of isobutene is proportional to the concentration of monomer, that of styrene proportional to the square of the monomer concentration [13], so that the same mechanism cannot apply to both monomers. Further, in the very system in which the Gantmakher and Medvedev mechanism would be most plausible, styrene - $SnCl_4$- nitrobenzene [10], the polymerization is found to be of first order in monomer and not, as Gantmakher and Medvedev predict, of second order, and moreover depended on the presence of water.

Details of our own results will be published shortly elsewhere. We thank Polymer Corporation of Canada and Esso Research, Ltd. for fund which made this work possible, and Mr. J. Forsyth for translating this paper into Russian.

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ON THE QUESTION OF THE MECHANISM OF THE INITIATION OF CATIONIC POLYMERIZATION IN THE PRESENCE OF METAL HALIDES

A. R. Gantmakher, Academician S. S. Medvedev and E. B. Lyudvig

The mechanism of the initiation of carbonium-ion polymerization in the presence of metal halides has been investigated by numerous authors. At the present time, there exist 2 different treatments of the mechanism of formation of the initial carbonium ion in these processes. According to one of these theories, cationic polymerization in the presence of metal halides cannot take place without the addition of various cocatalysts, while according to the second theory, cationic polymerization can proceed without the addition of cocatalysts under certain conditions. Moreover, the question of the nature of the cocatalysts has undergone considerable evolution with the development of work in this field.

Plesch, Skinner, Polanyi, Evans, and Meadows [1,2,3], while studying the cationic polymerization of isobutylene, both liquid and in solution in hexane, with $TiCl_4$ and BF_3 catalysts, established that polymerization does not occur unless a proton-containing promoter is present.

On the basis of their results, it was concluded that initiators of cationic polymerization are always proton-containing acids of the type $HB{\cdot}PX_n$ (HB is the cocatalyst, PX_n is the metal halide). These experiments were carried out under low-temperature conditions in media of low dielectric constant. However, their results on the polymerization of isoprene and of styrene in the presence of $SnCl_4$ showed that at higher temperatures and in media of higher dielectric constant, cationic polymerization can proceed without the addition of a cocatalyst [4].

That, as established by us, polymerization can proceed in alkyl halide solvents, dichloroethane, without the addition of a proton-containing cocatalyst [7,8,11] has been further confirmed by the work of Plesch [5] and Colclough and Dainton [6]. However, these authors, on the grounds that cationic polymerization can take place only with the participation of a cocatalyst, assume that in this case the role of the cocatalyst is fulfilled by the solvent according to the following schemes

$$RX + PX_n \rightarrow RX{\cdot}PX_n$$

$$RX{\cdot}PX_n + M \rightarrow R^+M{\cdot}PX_{n+1}^- \quad \text{(initiation)}$$

$$R^+M{\cdot}PX_{n+1}^- + M \rightarrow R^+M_2{\cdot}PX_{n+1}^- \quad \text{(growth)}$$

$$R^+M_m{\cdot}PX_{n+1}^- \rightarrow RM_mX + PX_n \quad \text{(breaking)}$$

where RX is an alkyl halide, M is the monomer, and PX_n is the metal halide.

It follows from this scheme that the chain-breaking reaction in such solvents as ethyl chloride and dichloroethane and with $TiCl_4$ or $SnCl_4$ as the catalyst should not depend on whether the process is carried out in the presence or absence of HCl, since in either case the carbonium ion exists in the field of the same anion.

This contradicts the results of our investigations in which it was shown that the addition of HCl decreases the molecular weight of polymers formed when the polymerization is carried out in alkyl halides and other solvents [7]. Moreover, only those HCl molecules which are combined with the catalyst have an effect.

These data, and also the results obtained by us on the kinetics of the polymerization and copolymerization

of various monomers [8,9,10,11], led us to the conclusion that in alkyl halide solvents, cationic polymerization can proceed directly under the influence of aprotic acids without the participation of compounds with the specific function of a cocatalyst.

In one of their recent researches, Longworth, Plesch, and Rutherford [12] investigated the $TiCl_4$-catalyzed polymerization of isobutylene and styrene in dichloromethane, and they came to the conclusion that in these systems, polymerization proceeds only in the presence of water as a promoter.

However, as these authors remarked, it was shown in the previous work of Plesch [5] and of Colclough and Dainton [6] that the metal-halide-catalyzed polymerization of styrene in dichloroethane can proceed without the addition of proton-containing cocatalysts. Moreover, Longworth, Plesch, and Rutherford [12] consider that the data on the kinetics of polymerization in these systems do not controvert the possibility of initiation occurring without the participation of a cocatalyst, since even if there were a cocatalytic action by the solvent in certain systems, this would not exclude the possibility of the simultaneous occurrence of initiation by interaction of the monomer with the catalyst without the participation of a cocatalyst.

The initiation reaction in the system monomer – catalyst apparently proceeds through the formation of a π-complex of the catalyst with the monomer. On the basis of the acceptor – donor properties of the catalyst and monomer molecules, and also on the basis of data obtained by us on copolymerization kinetics [10,11], we propose that the catalyst is present in the monomer solution as a complex with the monomer. Initiation of the reaction is accomplished by the interaction of this complex with the monomer [8, 13]:

$$PX_n \cdot M + M \rightarrow PX_n^- - M_2^+$$

A similar point of view on the mechanism of initiation without the addition of a cocatalyst has been presented in the papers of Okamura and Higashimura [14].

The formation of π-complexes of unsaturated compounds with tin tetrachloride was recently demonstrated for cyclohexene by Terenin, Filimonov, and Bystrov [15] by means of infrared spectroscopy.

It was shown that the frequency of the double bond in cyclohexene is decreased by 115-125 cm^{-1} by the interaction of the π-electrons of the double bond with $SnCl_4$.

The existence of π-complexes of unsaturated compounds with $SnCl_4$ also follows from data obtained by us during an investigation of the kinetics of the copolymerization of styrene with small amounts of more active monomers – α-methylstyrene and isobutylene [11].

It was shown that small amounts of α-methylstyrene or isobutylene (~ 0.02 mole fraction with respect to the styrene) sharply increases the rate of initiation of $SnCl_4$-catalyzed polymerization in ethyl chloride.

These data indicate the presence of a selective complex formation of the more active monomers, α-methylstyrene and isobutylene, with the catalyst, which causes a sharp increase in the rate of initiation in these systems.

It was established [11] that these effects are inhibited by the addition of water or HCl, which themselves form stable complexes with the $SnCl_4$; as a consequence of this, the formation of π-complexes of the monomers with the catalyst does not take place under these conditions.

It should be noted that certain authors, during investigations of cationic polymerization of styrene with $SnCl_4$ catalyst in various polar solvents [16,7,14,6], have observed an induction period, during which polymerization does not take place.

Okamura and co-workers [14] consider that the inverse proportionality which they observed to exist between the length of the induction period and the monomer and catalyst concentrations is due to a decrease in the rate of formation of monomer – catalyst complexes in solvents with low polarity.

Our data also support this view; according to these data, there is practically no induction period in the $SnCl_4$-catalyzed polymerization of α-methylstyrene in CCl_4 (concentration of α-methylstyrene, 2.5 moles/liter; concentration of $SnCl_4$, 0.006 mole/liter; temperature, 0°), while the polymerization of styrene under these conditions has a considerable induction period.

These data also indicate that α-methylstyrene is a better complex former with $SnCl_4$ than is styrene, owing to which the formation of complexes of $SnCl_4$ with α-methylstyrene proceeds at a considerable rate even in a nonpolar solvent.

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A UNIFIED ACIDITY SCALE

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In evaluating the acidity of nonaqueous solutions, the necessity arises of comparing the acidities of solutions in the same nonaqueous solvent and in different solvents.

The determination of relative acidity within the bounds of a single nonaqueous solvent does not differ in principle from the determination of pH in aqueous solutions. The value of pH_s in nonaqueous solutions is given by the negative logarithm of the activity of the lyonium ions MH^+, of the given solvent s

$$pH_s = -\lg a^{\circ}_{MH^+} = -\lg m_{MH^+}\,\gamma^{\circ}_{MH^+} \qquad (1)$$

In this equation, the activity $a^{\circ}_{MH^+}$ and the concentration activity coefficient γ_{MH^+} are referred to infinitely dilute solution in the given nonaqueous solvent. Owing to the difference in the products of the ion concentrations, the extension of the pH scale in nonaqueous solvents is different (see Figure 1), and we denote the specific acidity scale in nonaqueous solvents by the subscript s, pH_s which indicates pH of the neutral solution.

The measurement of pH in nonaqueous solutions can be carried out in the same manner as in water, but the measurement is made against a standard solution with a known pH_s in the same nonaqueous solvent. Standardization of the pH_s scale in nonaqueous and mixed solutions may be based on the concentration activity coefficients, γ° of the ions from hydrogen chloride [2].

Comparison of acidities in different solvents, in other words, reducing the pH_s scales to the same starting point, differs in principle from the comparison of acidities within a single solvent, since in this case the comparison must be made among acidities created by the different lyonium ions. In principle, as Brönsted has already shown [3], the acidity of a solution is uniquely determined by the activity of the protons in the solution. In order to evaluate the real acidity, not only is it necessary to determine the activity (concentration) of lyonium ions, but it is also necessary to establish the relative activity of the protons in the different lyonium ions. Moreover, as we have shown, it is convenient to select the proton activity in an infinitely dilute aqueous solution as the standard state. Thus

$$pA = -\lg a_{H^+} = -\lg a^{\circ}_{MH^+} - \lg \gamma_{OH^+} = pH_s - \lg \gamma_{OH^+}. \qquad (2)$$

In this equation, a_{H^+} is activity and γ_{OH^+} is the degenerate activity coefficient, both referred to infinitely dilute aqueous solution as the standard state. This value of the activity coefficient γ_{OH^+} is determined by the change in the energy (isobaric potential) of the protons during their transfer from an infinitely dilute nonaqueous solution to an infinitely dilute aqueous solution. This energy is determined by the difference in the chemical energies of solvation A_{xH^+} of the protons in water and in the nonaqueous solvent.

$$\lg \gamma_{OH^+} = \frac{A_{x_{H^+H_2O}} - A_{x_{H^+M}}}{2{,}3\,RT} = \frac{\Delta A_{x_{MH^+}}}{2{,}3\,RT}. \qquad (3)$$

Inasmuch as data on the values of γ_{OH^+} have not yet become available, a series of rather unreliable assumptions [4] have been made in order to evaluate the acidity of nonaqueous solutions; these by-passed the solution of the question of the value of ΔA_{xH^+} of protons. Hammett proposed the function H_0, while Schwarzenbach [6] proposed the function $H(_)$. However, it is readily shown that neither of these functions actually express the real

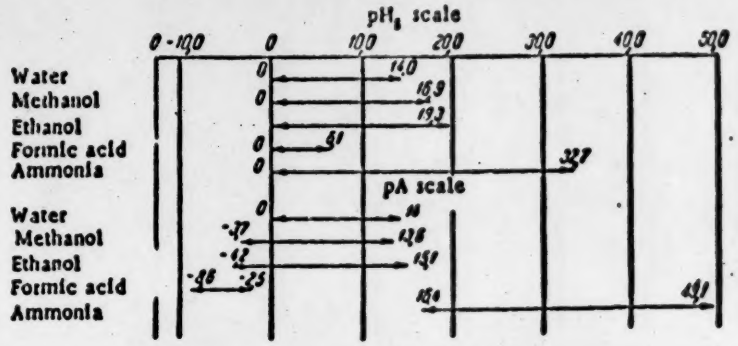

Fig. 1. Comparison of the acidity scales pH_s and pA.

acidity, since they are complicated by the degenerate activity coefficients of the single ions and molecules of the indicators.

$$H_0 = \lg a_{H^+} + \lg \frac{\gamma_{OBH^+}}{\gamma_{OB}};$$
$$H_{(-)} = \lg a_{H^+} + \lg \frac{\gamma_{OHA}}{\gamma_{OA^-}}. \qquad (4)$$

For the creation of a unified acidity scale, V. A. Pleskov [7] proposed to take the potential of the rubidium electrode as constant in all solvents and to evaluate the change in acidity by the change in the potential of the hydrogen electrode measured against the rubidium electrode.

Strelow [8] made an attempt to refine the proposal of Pleskov. For this purpose, he used the Born equation [9] to calculate the change in the energy of the rubidium ion during transfer from an aqueous to a nonaqueous solvent. The method of calculation and the values obtained for the change in acidity are not very reliable.

We propose to make use of the degenerate activity coefficients of hydrogen chloride [1] to evaluate the relative position of the pH_s scale. This proposal is based on the practically complete constancy of values of γ_0^{δ} of strong acids, which implies that the value of γ_0^{δ} of acids is related to the first order of the change in the solvation energy of protons.

Since we have determined the chemical energies involved in the solvation of ions, including the proton, in different solvents [10], it has now become possible to find the change in the energy of a proton during transfer from a nonaqueous solvent to water, and, consequently, to determine the value of $\lg \gamma_0$ and, in addition, the unique acidity of nonaqueous solutions, pA. In Table 1 are presented values of $\lg \gamma_{OH^+}$, calculated by the equation of reference [3], for methanol, ethanol, ammonia, and formic acid.

$$\lg \gamma_{OH^+} \approx 2 \lg \gamma_0^{base} + \lg \gamma_0^{el}. \qquad (5)$$

The value $2 \lg \gamma_0^{base} = \lg K_r + \lg \frac{a^{\circ}_{H_2O}}{a^{\circ}_{M}}$ is determined by the change in the basicity of the solvent. In the latter expression, K_r is the equilibrium constant for the exchange of protons between lyonium ions and hydroxonium ions, $K_r = \frac{a^{\circ}_{M} a^{\circ}_{H_3O^+}}{a^{\circ}_{H_2O} a^{\circ}_{MH^+}}$. This constant can be determined experimentally. The value γ_0^{el} is the average energy of solvation of lyonium ions and acid anions. On the basis of experimentally determined values of $\lg \gamma_0^{base}$ and $\lg \gamma_0$, it is possible to calculate γ_0^{el} and finally, the value of $\lg \gamma_{OH^+}$ [1,11]. It follows from Table 1 that the values of $\lg \gamma_{OH^+}$ obtained by this method agree with the values of $\lg \gamma_{OH^+}$ obtained directly from the difference in the solvation energies of protons. In this same table are presented values of $\lg \gamma_{OH^+}$ in alcohols, calculated by this same method. The values of $\lg \gamma_{OH^+}$ in alcohols and formic acid are positive, and, consequently, the activity of protons in the lyonium ions of these solvents increases. In ammonia, $\lg \gamma_{OH^+}$ is negative and, consequently, the activity of protons in ammonium ions is lower than in water.

Values of $\lg \gamma_{OH^+}$ in ethanol-water mixtures calculated by equation (5) using the data of V. V. Aleksandrov and N. A. Izmailov [12] are in general agreement with the values of $\lg \gamma_{OH^+}$ calculated by Grunwald [13] on the.

TABLE 1

	Solvent				
	NH_3	H_2O	CH_3OH	C_2H_5OH	HCOOH
$\Delta A_{zH^+} = A_{zH^+H_2O} - A_{zH^+M}$	−21,0	0	5,0	8,0	12,0
$\lg \gamma_{OH^+}$	−16,6	0	3,3	4,2	8,5
$\lg \gamma_{OH^+} = 2\lg \gamma_O^{base} + \lg \gamma_O^{el}$	—	0	3,3	4,2	—

	NH_3	H_2O	CH_3OH	C_2H_5OH	C_3H_7OH	n-C_4H_9OH	i-C_4H_9OH	t-C_4H_9OH	$C_6H_5CH_2OH$	HCOOH
$\lg \gamma_{OH^+}$	−16,6	0,0	3,3	4,2	4,3	4,7	4,5	4,45	3,8	8,5

TABLE 2

Non-aqueous solvent, %	$\lg \gamma_{OH^+}$ in methanol-water mixtures	$\lg \gamma_{OH^+}$ in ethanol-water mixtures	
		our data	Grunwald's data
0	0	0	0
20	0,14	0,17	0,08
30	0,22	0,25	0,12
40	0,32	0,33	0,15
50	0,43	0,42	0,20
60	0,52	0,60	0,42
70	0,74	0,80	0,65
80	0,95	1,10	1,15
90	1,45	2,10	2,65
100	3,3	4,2	4,7

basis of an empirical relationship, discovered by him, between the strengths of neutral and cationic acids and the composition of the mixture (see Table 2).

We used the values of $\lg \gamma_{OH^+}$ to determine the relative position of the pH_s scale in the pA acidity scale. It is seen from Figure 1 that the pA values in ethanol solutions are distributed from −4.2 to +15.1, in methanol from −3.3 to +13.5, in formic acid from −8.6 to 2.5, and in ammonia from +16.4 to +49.1. It is seen Figure 1 that the most alkaline solutions in formic acid are more acid than the most acid solutions in water and that the most acid solutions in ammonia are more alkaline than the most alkaline aqueous solutions. It may not be supposed, however, that, for example, solutions of acids in ethanol will always be, at 4.2 pA, more acid than the corresponding aqueous solutions. The value of pA of solutions of acetic acid in ethanol differ little from the pH of the aqueous solutions; this is explained on the basis that the pK of acetic acid in ethanol is 5 orders of magnitude higher than in water. In other words, in ethanol the activity of protons in ethyloxonium ions is considerably higher than in hydroxonium ions, and this increases the acidity; however, the number of ethyloxonium ions in ethanol solution of acetic acid is considerably lower than in the corresponding aqueous solution, and this decreases the acidity.

As an illustration of the relationship between pH_s and pA values, Figure 2 presents data for solutions of hydrochloric acid and acetate buffer in mixtures of ethanol and water. It follows from the figure that the pH_s value of a dilute solution of HCl is practically unchanged by a transfer from water to alcohol. This is a result of the fact that in the concentrations investigated, HCl remains a strong acid in all solvents. On the contrary, the pA values of these solutions, in conformity with the increase in $\lg \gamma_{OH^+}$, sharply decrease on going from water to alcohol.

Quite otherwise is the change in acidity of acetate buffer. Owing to the decrease in the strength of acetic acid, the value of pH_s increases greatly with an increase in the alcohol content, while owing to the simultaneous increase in $\lg \gamma_{OH^+}$, the value of pA changes slightly, increasing somewhat toward pure alcohol. The increase in $\lg \gamma_{OH^+}$ and the decrease in $\lg K_{diss.}$ are mutually compensating.

In this same figure are presented the acidity functions H_0 and $H_{(-)}$; it may be seen, however, that they do not characterize the true acidity of the nonaqueous solutions, and they occupy an intermediate position between the pH_s and the pA values.

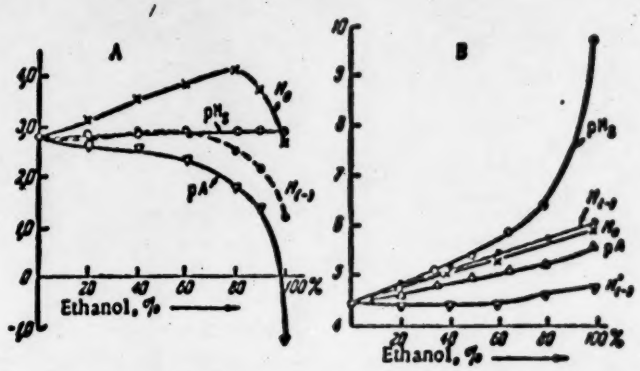

Fig. 2. Comparison of pH_2, pA, H_0, and $H_{(-)}$ values in mixtures of ethanol and water; A) solution of 0.002N HCl + 0.008N NaCl; B) buffer solution of 0.02N HAc, 0.01N Na Ac, 0.0005N NaCl; $H_{(-)}$ with 2,4-dinitrophenol, $H'_{(-)}$ with dimedon.

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KINETICS OF THE NUCLEOPHILIC REPLACEMENT OF CHLORINE IN PHENYL β-CHLOROVINYL KETONE

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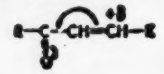
(Presented by Academician V. N. Kondrat'ev, March 9, 1959)

While the literature devoted to the mechanism of the nucleophilic replacement of a halogen atom attached to a saturated carbon atom is voluminous, data on the nucleophilic replacement of a halogen attached to an unsaturated carbon atom are very scant. As is well known, a halogen atom attached to a doubly bonded carbon atom in chlorovinyl-type compounds is very inert in substitution reactions. However, when any electrophilic group (CO, COOH, COOR, etc.) is present on the other side of the double bond, the halogen atom acquires high lability, and readily enters into nucleophilic substitution reactions.

These facts are well known with respect to substitution in β-chlorocrotonic acids and their derivatives [1], and have been particularly widely investigated with respect to β-chlorovinyl ketones [2]. The sharp increase in the the lability of the halogen atom in these cases is explained by an increase in the electrophilic character of the β-carbon atom, which facilitates nucleophilic attacks



However, the presently available data are purely qualitative, and they do not permit comparison of the lability of the halogen, either as a function of the activating group (CO, COOH, COOR, etc.) or as a function of the nature of the attacking nucleophilic reagent. Kinetic data are required for clarification of these questions.

A study of the kinetics of the nucleophilic replacement of the halogen atom in salts [3] and esters of the stereoisomeric β-chlorocrotonic acids was recently conducted in our laboratory, and it was shown that the substitution is a simple, irreversible bimolecular reaction. In a continuation of these investigations, which are essential for an understanding of the mechanism of nucleophilic substitution at an unsaturated carbon atom, we have studied the kinetics of the substitution of the chlorine atom in phenyl β-chlorovinyl ketone by an ethoxy group during the interaction of the ketone with sodium ethylate in alcoholic solution; it was previously shown that the phenyl β-chlorovinyl ketone was the trans isomer [4]. This reaction proceeds significantly more rapidly than the corresponding reaction of β-chlorocrotonic acids, and it leads to the formation of the β-ketoacetal.

The β-chlorovinyl ketone required for the investigation was prepared by a previously developed method [5], and was carefully purified by distillation. The kinetics of the reaction with sodium ethylate in alcohol were studied over the temperature interval from -5 to -30°. The flask containing the reaction mixture was placed in a thermostatted bath in which the temperature was maintained to within 0.1°. Methyl alcohol was used as the bath liquid. The bath was connected to a refrigerating chamber filled with solid carbon dioxide. A 0.1 N solution of phenyl β-chlorovinyl ketone in absolute ether was diluted with absolute ethyl alcohol and cooled in the bath to the temperature of the experiment; an alcoholic solution of sodium ethylate, precooled to the same temperature, was then added to the ketone solution, and the concentration of ketone in the reaction mixture was adjusted to 0.005 N. The sodium ethylate was always taken in excess, since it was partially consumed by secondary processes (formation of the acetal and other reactions); these side reactions had no essential effect on the results, since we followed the kinetics of the exchange process by measuring the concentration of halogen ion in the reaction mixture.

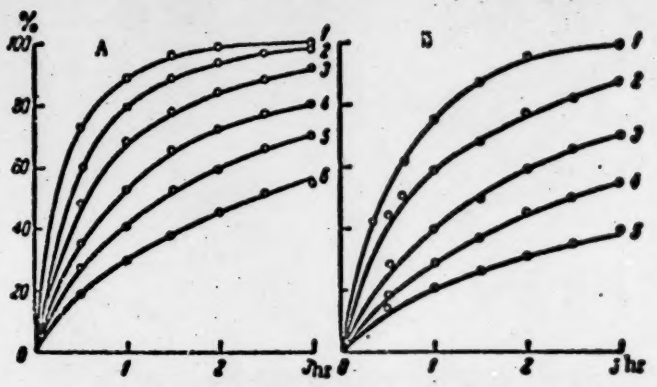


Fig. 1. Kinetic curves of the replacement of chlorine in phenyl-β-chlorovinyl ketone by an ethoxy group during the interaction of the ketone with sodium ethylate in ethyl alcohol: 1 at 5°; 2 at 10°; 3 at 15°; 4 at 20°; 5 at 25°; 6 at 30°. A) Sodium ethylate concentration 5 moles per mole of ketone (ethylate 0.025 N; ketone 0.005 N); B) sodium ethylate concentration 2.5 moles per mole of ketone (ethylate 0.125 N; ketone 0.005 N).

TABLE 1

Rate Constants for the Replacement of Chlorine in the Reaction of Phenyl β-Vinyl Ketone with Sodium Ethylate in Absolute Ethyl Alcohol at Different Temperatures

Concen. of solutions			−5°		−10°		−15°		−20°		−25°		−30°	
Sodium ethylate	Ketone	Time, min	chloride ion yield, %	K	chloride ion yield, %	K	chloride ion yield, %	K	chloride ion yield, %	K	chloride ion yield, %	K	chloride ion yield, %	K
0,0250 N	0,005N	30	73	1,92	60	1,31	48	0,92	35	0,59				
		60	89	1,63	80	1,19	68	0,83	53	0,54	40	0,35	29	0,23
		90	96	1,67	89	1,12	78	0,75	65	0,50	52	0,35	38	0,22
		120	99	1,82	94	1,09	84	0,69	72	0,47	60	0,33	45	0,21
		150			97	1,10	88	0,64	77	0,44	66	0,31	51	0,20
		180	100		98,5	1,10	92	0,69	80	0,40	70	0,29	55	0,19
		K_{av}		1,77		1,15		0,75		0,49		0,32		0,21
0,0125 N	0,005N	30			44	1,72	28	0,92	18	0,53	14	0,41		
		40			50	1,56								
		60			59	1,38	40	0,75	30	0,51	21	0,33		
		90			68	1,22	60	0,71	45	0,44	31	0,27		
		150			82	1,17	68	0,69	50	0,42	35	0,24		
		180			88	1,25	70	0,65	55	0,41	39	0,24		
		K_{av}				1,34		0,74		0,48		0,30		

The time at which the ketone and ethylate solutions were combined, with rapid and careful stirring, was taken as the beginning of the reaction. A series of experiments were carried out. Each experiment was stopped after a specified time interval. At the conclusion of an experiment, the reaction mixture was taken from the bath, diluted with water, and acidified with nitric acid. The acetal product and the other organic substances were separated by washing the reaction mixture with ether five times, and the chlorine content of the aqueous layer was determined by the Volhard method with the addition of nitrobenzene, which caused coagulation of the silver chloride precipitate and thus made possible a more accurate determination of the end point. The amount of chloride ion characterized the extent to which the exchange reaction had proceeded.

TABLE 2

Activation Energy for the Replacement of Chlorine by Ethoxyl During the Interaction of Phenyl β-Vinyl Ketone with Sodium Ethylate in Absolute Ethyl Alcohol at Different Temperatures

Temp., deg C	$\frac{10000}{T}$	$K \cdot 10^5$	$\lg(K \cdot 10^5)$
— 5	37,31	177	2,248
—10	38,02	115	2,060
—15	38,76	75	1,874
—20	39,52	49	1,690
—25	40,32	32,6	1,512
—30	41,15	21	1,322

E = 11.1 kcal/mole

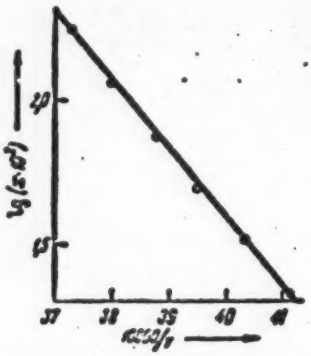


Fig. 2. Arrhenius plot for the reaction of phenyl β-chlorovinyl ketone with sodium ethylate.

The resulting kinetic curves are presented in Figure 1. The rate constant, calculated from these data by means of the equation for an irreversible bimolecular reaction, were practically constant.

As would be expected, a change in the initial concentration of sodium ethylate by a factor of two changed the reaction rate, but the value of the rate constant remained unchanged (see Table 1).

The activation energy calculated from these data is 11.1 kcal per mole. The preexponential term $K_0 = 4.10^7$ is lower by three orders than the usual value for a bimolecular reaction (see Table 2). Our data show that, as in the case of β-chlorocrotonic acids [3], exchange of the halogen atom in β-chlorovinyl ketones is a bimolecular reaction; this is in agreement with the previously proposed mechanism [2].

Thus, the nature of the activating group has no effect on the order of halogen-exchange reactions in compounds of the type of β-substituted vinyl halides. However, the nature of this group has a substantial effect on the rate of exchange of the halogen atom, as may be seen from a comparison of the activation energies for the substitution of an ethoxyl group for a halogen: the activation energy for the sodium salts of cis- and trans-β-chlorocrotonic acids is 23 kcal per mole, and for esters of cis-β-chlorocrotonic acid it is 17.6 kcal per mole, while for phenyl β-chlorovinyl ketone it drops to 11.1 kcal per mole. Thus, while the nature of the alkyl radical in the ester group of β-chlorocrotonic esters has no effect on the activation energy of the substitution reaction, replacement of the ester group by a ketone group has a sharp effect on the activation energy; naturally, this effect is connected with the more electrophilic character of the ketone group as compared to the ester group and the transfer of this effect to the β-carbon atom (see scheme on pg. 505.)

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CYCLOPROPANES AND CYCLOBUTANES IN THE DECOMPOSITION OF ALKYLTETRAHYDROPYRIDAZINES

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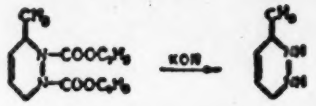
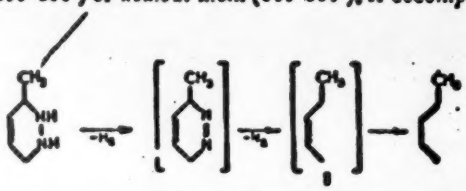
(Presented by Academician A. N. Nesmeyanov, February 18, 1959)

In previous reports [1,2], we have described the synthesis of arylcyclobutanes by a new method consisting of the decomposition of aryltetrahydropyridazines which, in turn, are obtained by hydrolysis of adducts of azodicarboxylic ester with arylbutadienes. Continuing this investigation, we attempted to use this method for the synthesis of alkylcyclobutanes.

Hydrolysis of the adduct formed from azodicarboxylic ester and piperylene gave a 3-methyltetrahydropyridazine. The latter was found to contain two NH groups (its dibenzoyl derivative was prepared), which indicates that during hydrolysis of the adduct the double bond does not shift to the nitrogen, as it does in the case of adducts of azodicarboxylic ester with arylbutadienes [2,3], but remains in the 4-positions



Although hydrolysis of the adduct did not yield 3-methyl -Δ^3- tetrahydropyridazine, it might be expected that, under the vigorous conditions under which the decomposition is carried out, shifting of the double bond to the nitrogen would proceed to yield 3-methyl-Δ^2-tetrahydropyridazine, which (analogously to 3-phenyl -Δ^2-tetrahydropyridazine [1,2]) would decompose to methylcyclobutane and nitrogen. However, our experiments showed that when 3-methyl -Δ^4-pyridazine is decomposed by heating, either in the presence of various catalysts (platinum, potassium hydroxide, or silver; 200-250°) or without them (300-350°), it decomposes to yield piperylene, nitrogen, and hydrogen according to



The intermediate biradical I is converted only to the diene (cyclization of the biradical to a cyclobutene is thermodynamically much less favored). It is possible that the reaction proceeds in a different manner--by decomposition of the 3-methyl -Δ^4- tetrahydropyridazine to piperylene and diimide, NH = NH, which immediately decomposes to nitrogen and hydrogen.

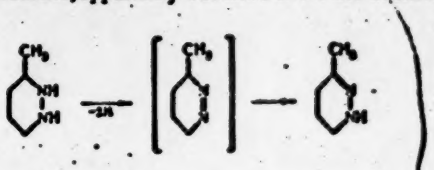
That even under the influence of such weak oxidizing agents as $CuCl_2$ $[Cu(NH_3)_4]Cl_2$ and HgO, 3-methyl-Δ^4-tetrahydropyridazine decomposes to nitrogen and piperylene supports the route first proposed. This decomposition also confirms that the double bond in the 3-methyltetrahydropyridazine formed by hydrolysis of the adduct is in the 4-position.

Similar results were obtained during a study of the decomposition of 3,4,5,6-bis (cyclopentano)- and 3,4,5,6-bis (cyclohexano) -Δ^4- tetrahydropyridazines, which are synthesized by hydrolysis of the adducts of azodicarboxylic

ester with 1,1'-bicyclopentenyl and 1,1'-bicyclohexenyl. These tetrahydropyridazines also contain two NH groups (they give dibenzoyl derivatives), and they decompose on heating in the same manner as the alkyl compound liberating nitrogen and hydrogen and forming, respectively, bicyclopentyl and bicyclohexyl.

We thus established that, starting with adducts of azodicarboxylic ester with alkylbutadienes or their non-aromatic cyclic analogs, it is impossible to obtain cyclobutane hydrocarbons in two stages, by hydrolysis of the adduct and subsequent decomposition of the resulting tetrahydropyridazine. Therefore, we decided to synthesize tetrahydropyridazines with the double bond at a nitrogen atom (decomposition of which should lead to cyclobutanes) by a circuitous route, oxidation of hexahydropyridazines.

3-Methyltetrahydropyridazine was synthesized by oxidation of 3-methylhexahydropyridazine. However, it proved to be not the expected 3-methyl-Δ^1-tetrahydropyridazine, but its isomer containing an NH group (it reacted with phenyl isothiocyanate to give the addition product). Isomerization of the azo form to the hydrazone form (to 3-methyl -Δ^2-tetrahydropyridazine) apparently occurred under the conditions of the reactions



Attempts to decompose the 3-methyl-Δ^2-tetrahydropyridazine under various conditions did not result in the formation of methylcyclobutane; either the original tetrahydropyridazine was recovered, or extensive decomposition accompanied by tar formation took place.

Similarly, oxidation of 3,4,5,6-bis (cyclopentano) hexahydropyridazine led to the formation of 3,4,5,6-bis (cyclopentano)-Δ^2- tetrahydropyridazine, which, on heating in the presence of catalysts, did not decompose with the evolution of nitrogen and the formation of tricyclodecane, but was instead recovered unchanged or was converted to tar.

Thus, it has been shown that alkyl-Δ^2-tetrahydropyridazines, in contrast to aryl-Δ^2-tetrahydropyridazines and pyrazolines, do not decompose on heating in the presence of catalysts to yield nitrogen and four-membered cyclic hydrocarbons.

EXPERIMENTAL PART

The Δ^4-tetrahydropyridazines were prepared by hydrolysis [4] of adducts of azodicarboxylic ester with piperylene, 1,1'-bicyclopentenyl, and 1,1'-bicyclohexenyl.

3-Methyl-1,2,3,6-tetrahydropyridazine: the yield was 63%; b.p. 63° (15 mm); n_D^{22} 1.4950; d_4^{22} 0.9735; MR_D 29.40. Calculated for $C_5H_{10}N_2$ 29.78*. The dibenzoyl derivative melted at 122° (from alcohol). Literature data [4]: b.p. 67° (18 mm); m.p. dibenzoyl derivative 121°.

3,4,5,6-Bis (cyclopentano) - Δ^4-tetrahydropyridazine: the yield was 28 % (after vacuum distillation); b.p. 132-135° (10 mm, with decomposition). The dibenzoyl derivative melted at 201-202° (from alcohol).

Found %: C 77.30; 77.33; H 6.40; 6.34
$C_{24}H_{24}N_2O_2$. Calculated %: C 77.39; H 6.50

3,4,5,6-Bis (cyclohexano) - Δ^4- tetrahydropyridazine: the yield was 54 %; m.p. 45-46° (from petroleum ether). The dibenzoyl derivative melted at 188-189° (from alcohol).

Found %: C 77.90; 77.83; H 7.00; 7.09
$C_{26}H_{32}N_2O_2$. Calculated %: C 77.97; H 7.05

Decomposition of the Δ^4-tetrahydropyridazines. 3-Methyl-Δ^4- tetrahydropyridazine was heated in an autoclave in the presence of potassium hydroxide for 2-8 hours at 200-250°. The gas evolved during the reaction was a mixture of nitrogen (~50%) and hydrogen (~ 50%) with small amounts of carbon dioxide (~0.3%) and unsaturated hydrocarbons (~ 0.5%). The liquid reaction product consisted of piperylene, piperylene dimer, and a small

* The atomic refraction of nitrogen was taken as 2.48 [5].

amount of tar. Piperylene: b.p. 41-42° (750 mm); adduct with maleic anhydride, m.p. 60°. Literature data [6]: b.p. 42.4-42.6° at 766 mm; adduct, m.p. 61°. Piperylene dimer: b.p. 155-162°; n_D^{20} 1.4710.

Found %: C 88.22; 88.29; H 11.80; 11.97.
$C_{10}H_{16}$. Calculated %: C 88.15; H 11.85

Literature data [7]: b.p. 58-59° (11 mm); n_D^{20} 1.4692.

When the reaction was carried out in the presence of platinum, the amount of hydrogen in the gas decreased and the liquid reaction product (b.p. 36-42°) contained 2-pentene and pentane along with the piperylene. The 2-pentene was characterized by preparation of the dibromide (after removal of the piperylene by treatment of the 36-42° fraction with maleic anhydride): b.p. 75-76° (14 mm); n_D^{20} 1.5070. Literature data [8]: b.p. 178° (748 mm); n_D^{20} 1.50783. The residue remaining after removal of the pentene and piperylene was n-pentane: b.p. 35.5-36.0° (755 mm); n_D^{20} 1.3572; d_4^{20} 0.6260. Literature data [9]: b.p. 36.00° (760 mm); n_D^{20} 1.35769; d_4^{20} 0.62624.

A vigorous reaction accompanied by the evolution of nitrogen and the formation of piperylene occurred when perhydrol was added to an aqueous solution of 3-methyl-1,2,3,6-tetrahydropyridazine in the presence of traces of cupric chloride; the yield of piperylene was 85%, b.p. 41.5-42.0° (755 mm), n_D^{20} 1.4304, d_4^{20} 0.6814; the adduct with maleic anhydride melted at 60-61°.

The decomposition of 3,4,5,6-bis (bicyclopentano) - and 3,4,5,6-bis (cyclohexano) - Δ^4 - tetrahydropyridazines was carried out by heating in a Wurtz flask. A vigorous reaction proceeded at 150-200° in the presence of potassium hydroxide or platinum and at 200-250° in the absence of catalysts. The gas evolved consisted of nitrogen (~ 50%) and hydrogen (~ 50%). Distillation of the reaction product gave the corresponding diene.

1,1'-Bicyclopentenyl: the yield was 68 %; b.p. 75-76° (7 mm); n_D^{20} 1.5260; adduct with maleic anhydride, m.p. 102-103°, literature data [10]: b.p. 78-79° (9 mm); n_D^{20} 1.5250; adduct with maleic anhydride, m.p. 102-103°.

1,1'-Bicyclohexenyl: the yield was 77%; b.p. 103-104° (7 mm), n_D^{20} 1.5334, adduct with maleic anhydride, m.p. 122-123°. Literature data [10]: b.p. 100-101° (5 mm); n_D^{20} 1.5329; adduct with maleic anhydride, m.p. 121-122°.

The Δ^2-tetrahydropyridazines were prepared by oxidation of the corresponding hexahydropyridazines (synthesized by hydrolysis of the hydrogenated adducts [4] of azodicarboxylic ester with piperylene and 1,1'-bicyclopentenyl) with perhydrol in the presence of traces of cupric chloride.

3-Methyl-Δ^2-tetrahydropyridazine: the yield was 82 %; b.p. 65° (16 mm); n_D^{20} 1.4880; d_4^{20} 0.9666; MR_D 29.27. Calculated for $C_5H_{10}N_2$ F 28.96*.

The product of the addition to phenyl isothiocyanate melted at 106° (from alcohol).

Found %: C 65.60; 65.57; H 6.70; 6.78; N 12.60; 12.70
$C_{12}H_{15}N_3S$. Calculated %: C 65.71; H 6.89; N 12.78

3,4,5,6-Bis (cyclopentano) - Δ^2 -tetrahydropyridazine: the yield was 67%; b.p. 121-122° (8 mm); n_D^{20} 1.5310; d_4^{20} 1.0592; MR_D 47.98. Calculated for $C_{14}H_{22}N_2$ F 47.65*.

The product of addition to phenylisothiocyanate melted at 149-150° (from alcohol).

Found %: C 67.99; 68.00; H 7.07; 6.96
$C_{17}H_{21}N_3S$. Calculated %: C 68.19; H 7.07

Decomposition of Δ^2 -tetrahydropyridazines. Attempts to decompose 3-methyl-Δ^2-tetrahydropyridazine were carried out both by heating at atmospheric pressure to the boiling point (both alone and in the presence of potassium hydroxide, platinum, silver, and cuprous chloride) and by heating in an autoclave. No reaction was detected when the compound was heated at 250° for three hours, and the original substance was recovered. On very long heating or with an increase in the temperature to 300-350°, tarring occurred accompanied by the evolution of a small amount of gas (~25% nitrogen, ~ 10% carbon dioxide, and ~ 50% unsaturated hydrocarbons). We were unable to separate a methylcyclobutane fraction by distillation of the reaction product.

3,4,5,6-Bis(cyclopentano)-Δ^2-tetrahydropyridazine oxidized very readily in air, even at room temperature.

* The molar refraction increment for the group $>N-N=$ was taken as 5.87 [11].

Evolution of nitrogen was not observed when the compound was heated to the boiling point under an atmosphere of CO_2 and in the presence of potassium hydroxide or platinum. It was almost completely converted to tar on prolonged heating (4-6 hours).

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A SPECTROSCOPIC INVESTIGATION OF α-METALLATED ALDEHYDES AND KETONES AND OF LITHIUM VINYLATE

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In a number of researches devoted to the study of reactions of α-mercurated aldehydes and ketones, it was established that these compounds are capable of exhibiting dual reactivity (at the C and at the O), thereby forming two series of derivatives. In one case, as in the reaction with triphenylchloromethane, the compounds formed correspond to direct substitution of the mercury atom; in other cases, as, for example, under the influence of acyl halides, the reaction proceeds with transfer of the reaction center as a consequence of the strongly expressed conjugation of the Hg—C and C = O bonds (σ - π conjugation).

σ - π conjugation is so well developed in α-metallated aldehydes and ketones owing to the presence of a metal atom of comparatively high polarizability (Hg, Sn). For this same reason, changes in the nature of the absorption of the carbonyl group would be expected in the vibrational and electronic spectra of these compounds.

We have carried out an investigation of the ultraviolet and infrared spectra in the absorption region of the carbonyl group of eight mercurated carbonyl compounds and of two ketones containing a tin atom alpha to the C = O group. Data from the infrared spectra, which were taken on an IKS-11 spectrometer, are presented in Table 1; the ultraviolet absorption maxima of these same carbonyl compounds are shown in Table 2 (data for acetaldehyde, isobutyraldehyde, and acetone are presented in the tables for comparison).

As may be seen from Table 1, the carbonyl group frequency is quite appreciably shifted under the influence of the mercury atom; the shift is commensurate with the shift of this band under the influence of conjugation of the C = O group with a double bond or with an aromatic ring (1680-1665 cm^{-1}) [4].

The ultraviolet absorption spectra of the mercury and tin derivatives of oxo compounds had an intense absorption band in the region characteristic of carbonyl compounds (280-300 mμ); hence, the shift of the characteristic band toward the long-wave region was insignificant, but there was a very strong increase in intensity (by a factor of 200-300).

TABLE 1

Position of the Absorption Band of the C = O Group in α-Mercurated Oxo Compounds

Compound	Frequency in cm^{-1}	Compound	Frequency in cm^{-1}
Isobutyraldehyde	1736	$C_6H_5COCH_2HgCl$	1660—1670
Acetone	1716	$C_5H_{11}COCH_2HgCl$	1660—1670
$(CH_3COCH_2)_2Hg$	1660	$Hg(CH_2CHO)_2$	1630—1650
CH_3COCH_2HgCl	1660	$ClHgCH_2CHO$	1680
$(C_2H_5COCH_2)_2Hg$	1660	$CH_3COCH_2Sn(C_3H_5)_3$	1688
$C_3H_7COCH_2HgCl$	1660—1670	$CH_3COCH_2Sn(C_4H_9)_3$	1684

TABLE 2

Absorption Maxima in the Ultraviolet Absorption Spectra of Carbonyl Compounds

Compound	λ, mμ	lg ε
CH_3CHO	293	1,07(*)
CH_3COCH_3	271	1,2 (*)
$Hg(CH_2CHO)_2$	296	2,90
$ClHgCH_2CHO$	300	2,60
$(CH_2COCH_3)_2Hg$	290	2,80
CH_3COCH_2HgCl	296	2,50
$(C_2H_5)_2SnCH_2COCH_3$	277—280	2,34
$(C_4H_9)_2SnCH_2COCH_3$	281—283	2,10

The data obtained from the infrared and ultraviolet spectra of α-metallated oxo compounds serve as a new argument in support of the existence in such compounds of σ - π conjugation, a phenomenon observed in a number of chemical reactions.

In addition to the spectra of α-metallated compounds of the type $RCOCH_2Me$ (1), where Me is Hg or Sn, we also studied the infrared and ultraviolet spectra of the simplest metal enolate with a structure isomeric with structure (1). The compound investigated was lithium vinylate, $CH_2 = CHOLi$, which was prepared from mercuridiacetaldehyde [6]. The infrared and ultraviolet spectra of this compound showed no absorption characteristic of the carbonyl group. On the other hand, a band of average intensity corresponding to the C = C double bond was found in the infrared spectrum at 1610 cm^{-1}; the appreciable shift of the absorption band of the double bond under the influence of the metal merits attention (from 1660-1640 cm^{-1} in vinyl ethers to 1610 cm^{-1} for lithium vinylate), and this shift is in good agreement with the shift in the band of a double bond conjugated with a phenyl or a carbonyl group (1600-1625 cm^{-1}) [4].

These results confirm the previous conclusion as to the C-structure of organomercury compounds prepared by addition of mercuriacetic acid to ethers and esters, and the O-structure of products of the cleavage of mercuridiacetaldehyde with the alkali metals.

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EXTRACTION OF RUTHENIUM NITROSONITRATE WITH ESTERS OF BUTYLPHOSPHONIC AND DIBUTYLPHOSPHINIC ACIDS

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Reports of work on the extraction of uranium, plutonium, and a number of other elements with new alkylphosphorus extractants have recently appeared in the literature [1,2,10]. The considerable interest in this class of compounds is caused by the fact that they have a greater capacity for extracting uranium and plutonium from aqueous solutions than does tributyl phosphate (TBP). L. I. Burger has established that in the transition along the series from TBP to dibutyl butylphosphonate (DBBP) to butyl dibutylphosphinate (BDBP), the distribution coefficient for plutonium increases in a regular manner [1], the values beings

	TBP	DBBP	BDBP
Pu^{IV}	1,57	32	170
Pu^{VI}	1,1	16	99

It is well known that ruthenium is one of the major fission products, and that it causes considerable difficulty in the recovery of uranium, thorium, and plutonium by contaminating the organic phase with β-and γ-activity [3]. The question of the behavior of ruthenium during extraction has been studied in sufficient detail only for TBP. Extraction with TBP has been studied by J. M. Fletcher [3,4], F. S. Martin [7], A. V. Nikolaev [5], and others, who investigated the dependence of the distribution coefficient of ruthenium during TBP extractions on the concentration of the extractant, the acidity of the aqueous phase, the valence state of the ruthenium, the temperature, and the concentration of ruthenium in the initial solutions. It has been established by the investigations of J. M. Fletcher [3], O. E. Zvyagintseva [6], J. Jenkins [8], P. G. Brown [2] , and others that in HNO_3 solutions obtained by dissolving uranium blocks in nitric acid, radioruthenium exists in the form of nitrosonitrate complexes.

For this reason, it seemed of interest to study the behavior of ruthenium nitrosonitrate during extraction with DBBP and BDBP, since even during extraction with TBP, contamination of the organic phase by radioruthenium has reached 70% in a number of cases [3].

In our experiments, the extraction was carried out in separatory funnels at a ratio of water to organic phase of 1:1. The initial solution of ruthenium nitrosonitrate, which was prepared by the method of O. E. Zvyagintseva and S. M. Starostin [6] contained 0.1 g per liter of carrier calculated on metallic ruthenium, and was 1 N with respect to nitric acid. Measurement of the γ-activity of the solutions was carried out by means of a scintillation counter with lead shielding 2 mm thick. Esters of butylphosphonic and dibutylphosphonic acids diluted with saturated high-boiling hydrocarbons (SHH) were used as the extractants. The phases were separated by centrifugation. The distribution coefficients were calculated by the equation,

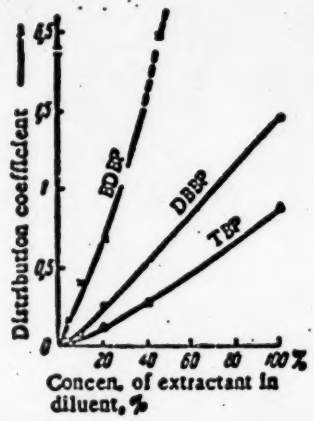
$$K_p = \frac{\text{Specific } \gamma\text{-activity of the organic phase}}{\text{Specific } \gamma\text{-activity of the water phase}}$$

The relative error in the determination of the distribution coefficients did not exceed ± 10%.

Preliminary experiments established K_p for ruthenium nitrosonitrate, prepared by the method indicated above, in extractions with TBP diluted with SHH. The results obtained are presented in Table 1.

TABLE 1

Extractant	Percentage content of extractant in diluent	Sp. activity of org. phase, imp./ min·ml	Sp. activity of aq. phase, imp./ min·ml	Per cent extraction	Distribution coefficient
$(C_4H_9O)_3P=O$	0	ΦОН	5990	0	0
	5	65	6000	1,07	0,011
	20	563	5300	9,6	0,11
	40	1260	4640	21,4	0,27
	100	2860	3290	48	0,87
$(C_4H_9O)_2(C_4H_9)P=O$	0	ΦОН	5590	0	0
	5	118	5500	2,1	0,024
	10	337	5490	5,8	0,062
	20	1200	4600	20,7	0,26
	100	3420	2300	59,8	1,48
$(C_4H_9O)(C_4H_9)_2P=O$	0	ΦОН	5400	0	0
	5	734	4720	13,5	0,16
	10	1580	3900	29	0,4
	20	2070	3260	38	0,64
	100	4380	672	87,8	6,5



On comparing the K_p values obtained for TBP extraction with those obtained for DBBP extraction, it is seen that there is no sharp difference in the behavior of ruthenium nitrosonitrate when one ester group is eliminated from the extractant molecule.

K_p for ruthenium nitrosonitrate was higher in BDBP than in TBP. A single extraction with undiluted BDBP gave 88% extraction of ruthenium, which corresponds to K_p=6.5

From the data obtained, which are presented graphically in Figure 1, it is seen that at low concentration of the extractants in SHH, K_p for ruthenium nitrosonitrate is about the same regardless of the ester used; it increased rapidly with an increase in the concentration of extractant, and the values in the pure extractants differed considerably.

Consequently, the extractants studied can be arranged in the following series with respect to increasing extraction of ruthenium nitrosonitrate into the organic phase: TBP < DBBP < BDBP. On the basis of these results it can be concluded that with a decrease in the number of ester groups in the extractant molecule, the reactivity of the free pair for electrons on the phosphoryl oxygen increases. This is explained by a decrease in the number of electron-acceptor groups ($-O-C_4H_9$) and by a shift of the electron cloud of the molecule toward the phosphoryl oxygen, which is the cause of the basic interaction with the substance being extracted. A similar regularity of increasing reactivity has been noted in the phosphine series

$$[R_3P > R_2POR > RP(OR)_2 > P(OR)_3 > PCl_3],$$

where R is saturated aliphatic radical [9].

Hence, it follows that by substituting a radical of higher electron-donor tendency [11]

$$[CH_3 < C_2H_5 < CH(CH_3)_2 < n\text{-}C_3H_7 < C(CH_3)_3],$$

for an ester group, it is possible to increase significantly the extractive capacity of organic solvents of the above class. This approach to the structure of extractants is undoubtedly of interest in the selection and synthesis of new extractants.

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TUNGSTATES OF ZIRCONIUM AND HAFNIUM

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Information available in the literature on zirconium tungstates is fragmentary and contradictory; hafnium tungstates are not described in the literature. Normal zirconium tungstate, $Zr(WO_4)_2$, a green, difficultly fusible substance, has been prepared by fusing together the calculated amounts of ZrO_2 and WO_3 in an oxyhydrogen flame [1]. The conditions required for the formation of hydrated zirconium tungstates of the compositions $5ZrO_2 \cdot 9WO_3 \cdot 33H_2O$ and $5ZrO_2 \cdot 7WO_3 \cdot 21H_2O$ [2,3] and the mixed salt zirconyl chloride tungstate $ZrCl_4 \cdot 2Zr(WO_4)_2 \cdot 2ZrO_2$ [4] are known. However, the existence of the latter compound as a chemical individual is not very probable. The literature contains no information on the properties and structures of zirconium tungstates, except for qualitative information on solubility and the results of chemical analyses.

The present work was devoted to the synthesis of hydrated and anhydrous zirconium and hafnium tungstates and to a study of some of their properties.

The hydrated zirconium and hafnium tungstates were prepared by the interaction of solutions of zirconyl or hafnyl nitrate and ammonium nitrate. The concentrations of the original solutions were 10 g/liter of ZrO_2 (or HfO_2) and WO_3. The solutions were poured together slowly and with stirring. The solutions were taken in such amounts that the molecular ratio of ZrO_2 (or HfO_2) to WO_3 was 1:1. Zirconium or hafnium hydroxide precipitated when the pH of the final solution was higher than 3.2. A colloidal white precipitate formed when the pH was in the range of 1.8 to 3.2, and this was coagulated by heating in 5% NH_4NO_3 solution. Analysis of the filtrates indicated that the initial substances had reacted completely. The precipitate was separated from the solution, carefully washed with water, and dried at 60° to constant weight.

The anhydrous zirconium tungstates were prepared by sintering zirconium (or hafnium) oxide or hydroxide with an equimolar amount of tungstic acid; the sintering was carried out for 6 hours at a temperature of 1100°. In order to avoid volatilization of WO_3, the furnace was heated to 1100° prior to the introduction of the reaction mixture. The formation of a new phase was checked by x-ray phase analysis. Quenching of the products from the sintering of the mixtures of ZrO_2 and WO_3 (1:1) and HfO_2 and WO_3 (1:1) resulted in the formation of white finely crystalline substances, the x-ray patterns of which were extremely similar and characterized by a peculiar collection of lines. The compounds were not formed when the sintered masses were cooled slowly. When the ZrO_2 (or HfO_2) and WO_3 were sintered in other ratios, for example, 1:2, 1:3, and 2:1, 1:1 compounds were formed containing an excess of one component or the other. New lines indicating the existence of substances with other ratios of oxides were not observed on the x-ray patterns.

Analysis of these compounds was carried out by the alkaline fusion and pyrosulfate fusion methods. In the first method, the substance was fused with a 1.5-2-fold excess of solid NaOH until a transparent melt formed. The cooled melt was leached with hot water; tungsten was determined in the solution, and the residual zirconium hydroxide was calcined at 800-900° and weighed. In the second method, the substance was fused with a 10-15-fold excess of potassium pyrosulfate, and the cooled transparent melt was leached with hot water; the zirconium was determined in the solution, and the residue, $WO_3 nH_2O$ was calcined at 700° and weighed. The amount of water in the hydrated zirconium and hafnium tungstates was determined by the weight loss when the substance was calcined at 700° to constant weight. The average results (from 5-6 experiments) of the analyses of the compounds are presented in Table 1. In accordance with the analytical data, the following formulas are assigned to these compounds

TABLE 1

Compound	ZrO_2, %	HfO_2, %	WO_3, %	H_2O, %	Ratio $Zr(Hf)O_2 : WO_3 : H_2O$
Hydrated zirconium tungstate	31,33	—	61,80	6,87	0,98 : 1,00 : 1,46
Anhydrous zirconium tungstate	35,41	—	64,33	—	1,04 : 1,00
Hydrated hafnium tungstate	—	42,85	49,35	7,72	0,97 : 1,00 : 2,16
Anhydrous hafnium tungstate	—	48,06	52,63	—	1,01 : 1,00

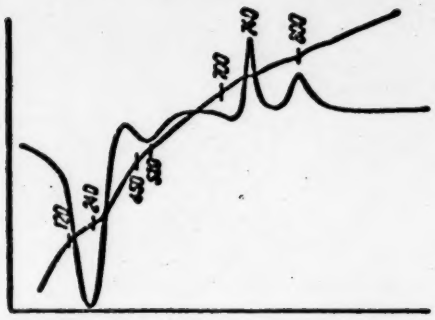

Fig. 2 Heating curve for $ZrOWO_4 \cdot 1.5H_2O$ (average rate of temperature rise, 12° per min).

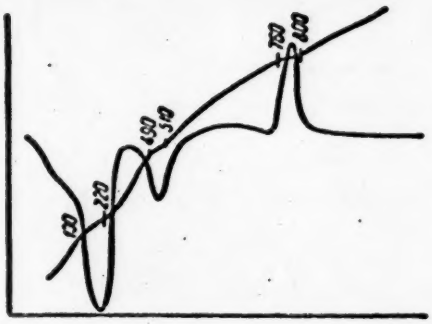

Fig. 3. Heating curve of $HfOWO_4 \cdot 2H_2O$ (average rate of temperature rise, 12° per minute).

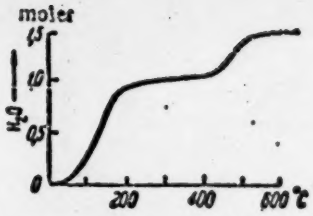

Fig. 1. Curve showing the change in weight of $ZrOWO_4 \cdot 1.5H_2O$ during heating (average rate of temperature rise, 10° per minute; sample weight, 0.9719 g).

$ZrOWO_4 \cdot 1.5H_2O$, $ZrOWO_4$, $HfOWO_4 \cdot 2H_2O$, $HfOWO_4$.

The hydrated zirconyl and hafnyl tungstates were white substances which, according to their x-ray patterns, were amorphous; they absorbed moisture from the atmosphere. The large number of lines (over 70) on the x-ray patterns of the anhydrous zirconium and hafnium tungstates indicate that either the crystal lattices of these compounds are of low symmetry or that at least one of the axial parameters has a high value. The high values of the glide angles are in conformity with the rather low densities: 5.27 for $ZrOWO_4$ and 6.27 for $HfOWO_4$. (The densities were determined pycnometrically at 25°).

In order to confirm that these compounds were chemical individuals and in order to compare their properties, their thermal stability, volatility with steam, and behavior toward different reagents were investigated.

The conversions which the zirconyl and hafnyl tungstates undergo when heated were studied with a Kurnakov pyrometer; the samples were suspended in a manner which permitted continuous weighing. Changes in the structures of the substances and the formation of new crystalline phases were determined by x-ray phase analysis. According to the curve showing the change in weight (Figure 1) and the heating curves (Figures 2 and 3), the dehydration of $ZrOWO_4 \cdot 1.5H_2O$ and $HfOWO_4 \cdot 2H_2O$ proceeded in two stages; one mole of water was lost in the temperature interval 80-240°, and the remaining water was lost at 450-550°. The loss of water proceeds without a change in the amorphous state of the substances. According to x-ray phase analysis, complete dehydration of the compounds was accompanied by decomposition to the oxides ZrO_2, HfO_2, and WO_3. In addition, monoclinic ZrO_2 and HfO_2 and the high-temperature rhombic modification of WO_3 crystallized in the temperature interval 740-800°; their formation was recorded on the thermograms of the zirconium and hafnium compounds as exothermic effects. Crystallization of ZrO_2 and WO_3 proceeded through a stage in which the low-temperature cubic form of ZrO_2 and monoclinic WO_3 were formed (exothermic effect at 700-740°). The anhydrous zirconyl and hafnyl tungstates decomposed to the oxides when heated to 800-850°. The heating curves of $ZrOWO_4$ and $HfOWO_4$ were much alike. The thermogram of $ZrOWO_4$, which is presented in Figure 4 as an example, clearly shows 2 effects. The first exothermic effect (850-900°) was due to decomposition of the substance, which proceeded with the formation of monoclinic ZrO_2 and rhombic WO_3. The endothermic effect (1150-1180°) was due to the reversible transition of the monoclinic modification of ZrO_2 to the tetragonal.

TABLE 2

Volatility of Zirconyl and Hafnyl Tungstates in a Current of Steam. Sample weight, 0.3 g; rate of steam feed, 4.5 ml/sq cm·hr; experiment time, 1 hour

Temperature, deg C	Weight loss, %							Ratio ZrO_2 (or HfO_2) : WO_3 in residue			
	WO_3	$ZrOWO_4$	$ZrOWO_4 \cdot 1.5H_2O$ moisture		$HfOWO_4$	$HfOWO_4 \cdot 2H_2O$ moisture		$ZrOWO_4$	$ZrOWO_4 \cdot 1.5H_2O$	$HfOWO_4$	$HfOWO_4 \cdot 2H_2O$
			8%	13%		8%	13%				
600	1.1	1.3	12.3	30.0				1.04 : 1	1.05 : 1		
700	1.7	1.2	14.6	31.5	0.3	12.6	41.5	1.05 : 1	1.06 : 1	0.98 : 1	0.99 : 1
800	2.2	2.5	17.4	39.2	2.6	26.4	51.8	1.30 : 1	1.24 : 1	1.02 : 1	1.01 : 1
900	6.1	7.6	21.3	50.9	6.9	27.7	60.3	1.39 : 1	1.35 : 1	1.04 : 1	1.09 : 1
1000	29.6	20.1	43.7	83.0	21.9	48.8	83.8	2.04 : 1	—	1.55 : 1	2.32 : 1

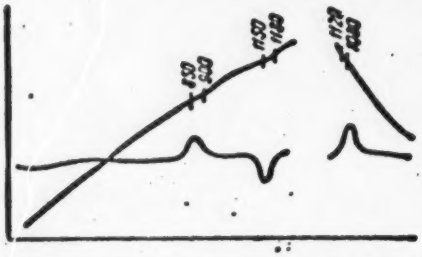

Fig. 4. Heating and cooling curves of $ZrOWO_4$ (average rate of temperature rise, 10°/minute).

TABLE 3

Behavior of Hafnyl and Zirconyl Tungstates Toward Reagents

Reagent	Amt. of dissolved substance, g/100 g of reagent	
	$ZrOWO_4$	$HfOWO_4$
HCl 36%	0.058	0.158
H_2SO_4 94%	0.068	0.128
H_2F_2 25%	0.310	0.332
NH_4OH 29%	0.024	0.086
NaOH 20%	0.330	0.240

The study of the steam volatility of these compounds was carried out at different temperatures in order to determine the temperature dependence. The apparatus used for this purpose has been described in previous papers [5]. All experiments were carried out under the same conditions. The substance, ground to a grain size of < 100 μ, was placed in a furnace preheated to the desired temperature. Distillation of the compounds and, for comparison, of WO_3 was carried out at 600, 700, 800, 900, and 1000°. At the conclusion of an experiment, the amounts of ZrO_2 or HfO_2 and WO_3 in the residue were determined. The results are presented in Table 2, where the values given represent averages of 4-5 determinations. The hydrated zirconium and hafnium tungstates are rather highly volatile with steam, and the volatilities of these compounds increase with an increase in the bound-water contents of the compounds. At 700° where both compounds distill without decomposition, the size of the fractions of $ZrOWO_4 \cdot 1.5H_2O$ and $HfOWO_4 \cdot 2H_2O$ distilled were 13-11% (8% moisture) and 30-40% (13% moisture) greater than that of WO_3. An increase in the temperature led to decomposition of the substances, but the hafnium compound was characterized by a higher thermal stability than the zirconium compound. The volatility of the anhydrous tungstates was almost the same magnitude as that of WO_3. However, in this case also there was observed the same difference in stability of the zirconium and hafnium compounds. $ZrOWO_4$ and $ZrOWO_4 \cdot 1.5H_2O$ underwent decomposition as low as 800°, while $HfOWO_4$ and $HfOWO_4 \cdot 2H_2O$ were stable in a current of steam up to 1000°. The ratio HfO_2:WO_3 in the residue of distillations at 700-900° remained constant at 1:1.

The study of the behavior toward reagents was carried out with concentrated solutions of HCl (36%), H_2F_2 (25%), H_2SO_4 (94%), NaOH (20%), and NH_4OH (29%) at room temperature (18°) and with heating (85-90°). A specific weight of the substance (0.12-0.20 g) was treated with 50-100 ml of the reagent for 4 hours with periodic stirring. The residue was washed with water, dried at 100°, and weighed. In the case of the anhydrous tungstates, the residue was subjected to x-ray phase analysis. The investigations showed that the hydrated zirconyl and hafnyl tungstates interact with the reagents used considerably more readily than do the anhydrous compounds. Even in the cold, the samples of $ZrOWO_4 \cdot 1.5H_2O$ dissolved completely in NaOH and H_2F_2 solutions. In concentrated HCl and H_2SO_4 solutions, complete solution of the compound was attained only by heating. $ZrOWO_4 \cdot 1.5H_2O$ was considerably less soluble in NH_4OH than was tungstic acid (by a factor of 30). The anhydrous tungstates dissolved only to a certain extent in NaOH and H_2F_2, and then only when heated; both compounds were only very slightly soluble in concentrated solutions of H_2SO_4, HCl, and NH_4OH (Table 3). On interaction with HCl and H_2SO_4, zirconyl tungstate decomposed, while the hafnium compound remained unchanged. It should be pointed out that the rate of solution of $HfOWO_4$ was 3-4 times greater than that of $ZrOWO_4$.

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A COMPARISON OF KINETIC RELATIVE ADSORPTION COEFFICIENTS WITH RELATIVE ADSORPTION COEFFICIENTS DETERMINED BY MEANS OF THE BET EQUATION

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By developing the concepts of Langmuir, Brunauer, Emmett, and Teller [1], in 1939, derived an equation for multilayer adsorption taking into account adsorbent-adsorbate interaction in the first layer and pertaining to adsorption over the entire surface; the BET equation may be written:

$$\frac{p}{a(p_s-p)} = \frac{1}{a_m c} + \frac{c-1}{a_m c}\frac{p}{p_s} \qquad (1)$$

The adsorption coefficient c may be determined by a graphical solution of Equation (1) by plotting $\frac{p}{a(p_s-p)}$ against $\frac{p}{p_s}$. In 1942, one of us [2] derived a kinetic equation for unimolecular reactions in a flow system, the equation being based on the assumption of a Langmuir adsorption isotherm; a method has also been proposed for the calculation of relative adsorption coefficients from kinetic data [3], and this permits determination of these coefficients for the catalytically active centers of the surface.

Later a kinetic equation of unimolecular reactions in a flow system was developed without any assumptions as to the form of the adsorption isotherm [4]. This equation differed from the equation of reference [2] only in that, as shown in reference [4], the relative adsorption coefficients entering into this later equation may relate to any form of adsorption isotherm: Langmuir, Temkin, BET, etc. Kinetic methods for the determination of relative adsorption coefficients have been considered in detail in reference [5].

Equation (2) may be used for the determination of relative adsorption coefficients from kinetic data; this equation is identical to Equation (52) of reference [5].

$$m = \frac{A_1 K}{\sum z_r A_r + \frac{K}{2}}, \qquad (2)$$

where m is the number of moles reacted, A_r is the number of moles of the rth substance admitted to the reactor, K is the rate constant, and Z_r is the relative adsorption coefficient of the rth substance. Equation (2) is quite accurate up to 30% conversion. Equation (1) assumes that the surface is homogeneous, while Equation (2) applies both for homogeneous and for quasihomogeneous surfaces [6].

It is interesting to compare relative adsorption coefficients obtained by means of Equation (1) with relative adsorption coefficients calculated by Equation (2). Using a somewhat different method for the solution of the kinetic equation for unimolecular reactions in a flow system, T. V. Antipina and A. V. Frost [7] carried out a detailed comparison of absolute adsorption coefficients for the dehydration of ethyl alcohol over aluminum oxide. The authors came to the conclusion that the absolute adsorption coefficients differed by two orders of magnitude. Hence, it was concluded that the adsorption and catalytic centers differ in nature. Recently, K. V. Topchieva and B. V. Romanovskii [8], by more carefully drying the ethylene, obtained kinetic adsorption coefficients which differed from those reported in reference [7].

TABLE 1

Catalyst	c_{BET} benzene	c_{BET} cyclohexane	z_{BET}	z_k from Equation (2)
	1	2	3	4
No.1 Ni/Al_2O_3	88,5	22,1	4,0	4,05
No.2 Ni/silica gel	22,0	2,93	7,3	6,0
No.3 Ni/Al_2O_3, Al_2O_3 from the acetate	8,5	4,1	2,1	2,0
No.4 Ni/kieselguhr	29,0	14,1	2,1	2,15
No.5 Ni/Al_2O_3, Al_2O_3 Industrial	15,1	7,4	2,05	2,05

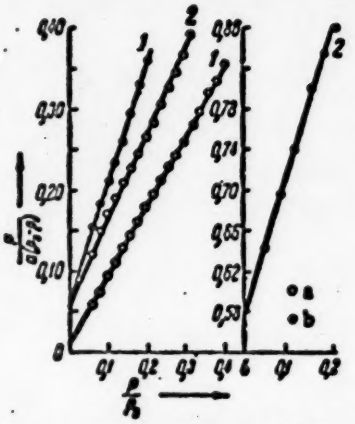

Fig. 1. BET adsorption coefficients for Catalysts Nos. 1 (1) and 2 (2). a) benzene; b) cyclohexane.

As a subject for our investigation, we selected the dehydrogenation of cyclohexane over supported Ni catalysts. The catalysts were prepared by impregnation of the carrier with $Ni(OH)_2$ with subsequent drying in a drying cabinet at 110° and reduction in a stream of hydrogen by the method described in reference [9]. The $Ni(OH)_2$, in turn, was prepared by precipitation from a molar solution of nickel nitrate with a 20% solution of NaOH. The precipitate was washed free of NO_3' ions with distilled water (negative test with diphenylamine). Catalyst 1 was prepared differently by coprecipitation from a solution of the calculated amounts of Ni and Al nitrates with a 20% solution of NaOH. After the precipitate had been washed to a negative test for NO_3', it was treated identically to the other catalysts. The nickel content of all catalysts was 23.5 wt. %. The adsorption isotherms were determined by a gravimetric method [10] using a quartz spring balance.

The BET adsorption coefficients were determined by graphical solution of Equation (1). By way of example, the curves for Catalysts Nos. 1 and 2 are presented in Figure 1. As is well known, the intercept with the ordinate gives the value of $\frac{1}{a_m c}$, and the slope of the line is equal to $\frac{c-1}{a_m c}$. From these values, the BET adsorption coefficients (c_{BET}) for benzene and cyclohexane were calculated; the ratio of these coefficients is the BET relative adsorption coefficient (z_{BET}) (see Table 1, Columns 1, 2, and 3). The kinetic relative adsorption coefficients were calculated by means of Equation (2).

The dehydrogenation of cyclohexane was carried out in a flow system by a previously described method [10]; the amount of catalyst (volume V) was such that the conversion did not exceed 30%. An experiment with pure cyclohexane was carried out first; in this case, Equation (2) transforms to

$$m = \frac{A_1 K}{A_1 + K/z} \qquad (3)$$

An experiment with a mixed feed was then carried out at the same temperature; the total number of moles of feed remained constant in these experiments. Another experiment with pure cyclohexane was then carried out to confirm that there had been no catalyst poisoning. Theoretically, the rate constants K in Equations (2) and (3) should be identical for an uncomplicated case. This was experimentally observed in the work of one of us together with Yu. K. Yur'ev [11], according to which the energy of activation for the dehydrogenation of xylene-dimethylcyclohexane mixtures over Ni/Al_2O_3 catalyst did not change for mixtures containing down to 10% dimethylcyclohexane. This observation was confirmed by us for benzene-cyclohexane mixtures over Catalyst No. 3.

Values of the relative adsorption coefficient for benzene as determined from adsorption and from kinetic data are presented in Columns 3 and 4, respectively, of Table 1. It is noteworthy that the values of these two series are close to the same. The slight divergence in the case of the Ni-on-silica-gel catalyst may well be due to a dependence of the kinetic relative adsorption coefficient on mixture composition for mixtures rich in benzene, a dependence actually observed for this catalyst (see Table 2).

Thus, the BET equation is applicable in the case of cyclohexane dehydrogenation over supported Ni catalysts (see Figure 1), and, within the limits of mixture composition investigated, the general kinetic equation for unimolecular reactions in a flow system from reference [4] is justified, as is apparent from the constancy of z in Table 2. The relative adsorption coefficients of the catalytically active centers were practically the same as the relative adsorption coefficients for the entire surface.

TABLE 2

Catalyst	T, °C	% C_6H_{12} in mixture with C_6H_6	z_k	av.
No. 1 V = 6 ml	271	29,8	4,01	4,05
		43,5	4,09	
	289	65,5	3,99	3,95
		43,5	4,12	
		29,8	3,73	
	302	29,8	4,15	4,15
No. 2 V = 16,5 ml	277	43,5	~14	—
		65,5	5,53	6,12
		82,6	6,71	
	292	82,6	6,59	5,94
		89,9	5,94	
		82,6	5,29	
	308	43,5	~22	—
No. 3 V = 5 ml	280	29,8	1,99	2,00
		65,5	2,10	
		43,5	2,01	
		65,5	1,97	
No. 4 V = 6 ml	271	29,8	1,90	2,15
		82,6	2,74	
		43,1	2,13	
		65,5	2,04	
	292	65,5	2,09	2,09
	314	65,5	2,64	2,17
		29,8	2,02	
		65,5	2,19	
No. 5 V = 5,5 ml	282	29,8	2,02	2,08
		65,5	2,08	
		43,5	2,08	

The equality Z_k and BET can be considered as confirmation of the concept proposed by one of us [12] that sites with an average adsorption strength are the catalytically active sites.

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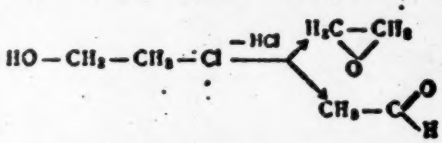
ON THE MECHANISM OF THE FORMATION OF ALDEHYDES DURING DEHYDROCHLORINATION OF LOWER ALKYLENE CHLOROHYDRINS

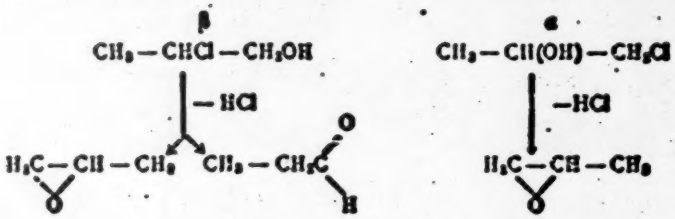
P. V. Zimakov and L. M. Kogan

(Presented by Academician B. A. Kazanskii, April 1, 1959)

We have previously shown that the conversion of lower alkylene chlorohydrins (ethylene chlorohydrin, propylene chlorohydrin) to the corresponding α-oxide or aldehyde

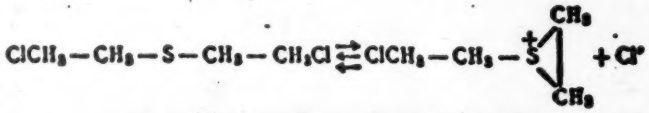


proceeds with good yields, the product depending on the nature of the medium in which the reaction is carried out [1]. Of the two isomers of propylene chlorohydrin, only the β-isomer can be converted to the aldehyde; the α-isomer is not capable of undergoing such conversion

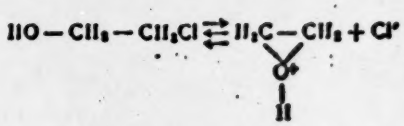


The conversion of lower alkylene chlorohydrins to α-oxides proceeds by the Wurtz reaction in media of high pH, such as solutions of alkalies or suspensions of alkaline earth metal hydroxides ("milk of lime"). Conversion to aldehydes proceeds especially smoothly in a suspension of nickel hydroxide [1]. It has been claimed that an appreciable yield of aldehydes is obtained by decomposition of alkylene chlorohydrins in a medium of "milk of magnesia" [2]. Certain considerations relating to the probable mechanism of the similar dual reactivity of such simple compounds as the lower alkylene chlorohydrins are presented below.

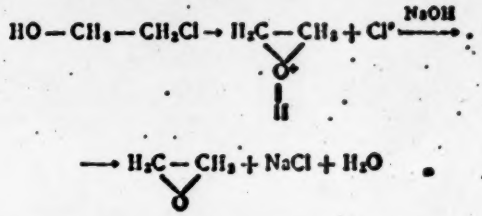
The alkylene chlorohydrins have two easily polarizable atoms, Cl and O, which are located β- to each other. Such a disposition promotes their mutual effect on each other, which is frequently accompanied by a change in the valence state of one or both atoms. An example of the special "activity" of such β- disposition of a chlorine and an easily polarizable sulfur atom is to be found in the yperite [β,β'-dichlorodiethyl sulfide] molecule, the peculiar toxicity of which is due to the ease with which the sulfur and chlorine atoms change valence [3].



Ethylene chlorohydrin (and propylene chlorohydrin), as a consequence of the peculiarities of its structure, is also a compound in which the polarizable atoms are very active. This is the reason for its reactivity. It is well known that, on long standing, even anhydrous ethylene chlorohydrin forms a certain amount of diethylene glycol chlorohydrin with the liberation of an equivalent amount of HCl [4]. Such a conversion is brought about by a transition of the individual molecules of the chlorohydrin to an "active" polar form with changes in the valence states of the oxygen and chlorine [5]



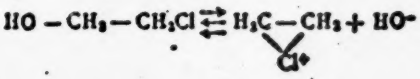
It was previously shown that the Wurtz reaction leading to the formation of ethylene oxide proceeds through precisely such an active form of the chlorohydrin molecule with an oxonium oxygen and ionic chlorine [6]



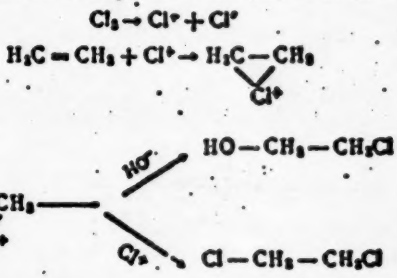
The formation of propylene oxide from propylene chlorohydrin proceeds by the same mechanism. In this, both propylene chlorohydrin isomers (α and β) react practically alike.

In actual practice, the ethylene oxide formed in the Wurtz reactions is always accompanied by a small amount of acetaldehyde [7]. One of the first to note this was Krasuskii [8], who also showed that the formation of acetaldehyde increases with a decrease in the alkalinity of the medium. In explaining the formation of acetaldehyde, Krasuskii assumed the addition of the elements of hypochlorous acid to intermediately formed ethylene oxide with the formation of the ethyl ester of hypochlorous acid.

At the present time, it may be considered probable that in media not containing an excess of hydroxyl ions, the ethylene chlorohydrin molecule can assume a second active, "chloronium", form with the elimination of a hydroxyl ion:



Such an assumption necessarily follows from the mechanism assumed by many investigators for the formation of ethylene chlorohydrin during the chlorination of ethylene in an aqueous medium [10]:



Analogous active forms, but with a different degree of stability, exist for the isomers of propylene chlorohydrin. Thus, the α-isomer, which is formed to the extent of almost 90% during the hypochlorination of propylene in aqueous medium, naturally has little tendency to go into the chloronium state; on the other hand, the β-isomer, which is formed to an extent of up to 10% during hypochlorination of propylene, relatively readily goes into the chloronium active state [11].

α $Cl-CH_2-\underset{OH}{CH}-CH_3$ —//→ Practically no chloronium is formed

β $HO-CH_2-\underset{Cl}{CH}-CH_3 \rightleftarrows HO^- + H_3C-\underset{Cl^+}{CH}-CH_3$

The actual behavior of the isomeric propylene chlorohydrins depends on their structures: in the α-isomer, the chlorine occurs β- to a methyl group, which increases its electronegativity, so that it cannot undergo transition to the chloronium state. On the other hand, the β-isomer has its methyl group α- to the chlorine, and this promotes its transition to the chloronium state, simultaneously increasing the tendency of the hydroxyl to be eliminated as an ion.

Krasuskii also noted that isomerization of α-oxides to aldehydes proceeds only in weakly acidic media [8]. This observation was later confirmed [12]. Hence, it is understandable that the formation of aldehydes during the elimination of the elements of HCl from alkylene chlorohydrins can take place only in those media which do not have an excess of hydroxyl ions. An aqueous suspension of nickel hydroxide is a particularly suitable medium [1]. Why is this medium particularly favorable for the formation of aldehydes? Nickel hydroxide, $Ni(OH)_2$, is only sparingly soluble in water, and does not impart a basic (alkaline) reaction to the solution (does not color turmeric paper). It can be assumed that the interaction of ethylene chlorohydrin with an aqueous suspension of nickel hydroxide at the boiling point proceeds through the following stages:

$$Ni(OH)_2 \rightleftarrows Ni=O + H_2O \quad (Ni \rightarrow O \rightarrow Ni^+ - O^-)$$

$$(Ni^+ - O^-) + \left\{HO^- H_2C-\underset{Cl^+}{CH}-CH_3\right\} \rightarrow Ni\begin{matrix}OH\\ O-CH-CH_3\\ \quad Cl\end{matrix}$$

$$Ni\begin{matrix}OH\\ O-CH-CH_3\\ \quad Cl\end{matrix} \rightarrow Ni\begin{matrix}OH\\ Cl\end{matrix} + O=CH-CH_3$$

Similar alcoholate forms of nickel compounds have been described by Reppe in connection with the catalytic isomerization of olefins in the presence of nickel chloride and ethylene oxide [13].

The great tendency to form a basic chloride is an intrinsic property of nickel, and the intermediate compound with the alkylene chlorohydrin readily loses a molecule of acetaldehyde to form the basic nickel chloride. The α-isomer of propylene chlorohydrin, which has no tendency to split off a hydroxyl and to form a chloronium ion, does not generally react with an aqueous suspension of nickel hydroxide [1]. In alkaline media, this does not prevent the α-isomer from forming propylene oxide in good yield, the reaction proceeding through the intermediate oxonium form. It is evident that in a medium of "milk of magnesia" where the yields of α-oxide and aldehyde are approximately equal [14], both reaction chains proceed in parallel.

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INFRARED SPECTRA OF FERROCENES. CONTRIBUTION TO THE QUESTION OF THE MUTUAL EFFECT OF SUBSTITUENTS IN THE FERROCENE MOLECULE

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(Presented by Academician A. N. Nesmeyanov, February 21, 1959)
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It has recently been shown that the mutual effect of substituents is effectively transmitted throughout the entire ferrocene system from ring to ring [1-3]. This conclusion was formed on the basis of a comparison of the dissociation constants of ferrocene carboxylic acids of the type $Y-C_5H_4-Fe-C_5H_4-COOH$. As a result of this study, the substituents were arranged in the following order with respect to their effects

$$C_4H_9 < C_2H_5 < H < COOCH_3 \leqslant COCH_3 < CN < SO_2NH_2 < SO_2F, \qquad (1)$$

where the substituents to the right of hydrogen increase the dissociation constant of the carboxyl and those to the left decrease it.

The mutual effect of substituents in the ferrocene system on the infrared spectra is apparent as a change in the frequency of a sustituent in one ring under the influence of different substituents in the other ring of the molecule. As a consequence of the fact that the carbonyl frequency is characteristic to a high degree, it was possible for us to carry out an infrared spectroscopic investigation of the series indicated above and to extend the investigation to esters of ferrocene carboxylic acids having different substituents in the other cyclopentadienyl ring.

The spectra of these compounds, which were obtained in the region covered by a NaCl prism using a paste of the material in vaseline oil, are presented in Table 1.

However, data on C = O frequencies obtained from compounds in the solid state are not very suitable for purposes of comparison. In solids, the frequency is shifted by intermolecular dipole-dipole interaction between the molecules in the crystal lattice, which has a very strong effect on the frequencies of such polar groups as the carbonyl group. Strong intermolecular interaction can significantly distort the picture due to intramolecular interaction. In addition to shifting the frequency, intermolecular interaction sometimes leads to splitting of the frequencies. Thus, three absorption bands were found for compounds 1 and 9, although there is only one C = O group in the first compound and only two in the second. Similar splitting was also found for compounds 6, 7, and 14, Table 1; this considerably hinders frequency assignments.

In order to remove these additional effects caused by intermolecular interaction, we obtained the infrared spectra of the same compounds in solution. In spite of the fact that, in our case, carbon tetrachloride would have been the most suitable solvent (owing to its nonpolarity and slight interaction with the dissolved substance), we were forced to use chloroform, since most of the compounds studied are difficultly soluble in carbon tetrachloride. C = O group vibrational frequencies for the solid compounds and for solutions are presented in Table 2.

It is apparent from Table 2 that the carbonyl group frequency changes with the transition from the solid state to solution. The frequency splitting observed for the solid state disappeared for solutions, although for compound 8 one of the carboxyl bands was, nevertheless, diffuse, probably owing to interaction with the solvent.

TABLE 1

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
832 l 854 W 880 W 898 aV	844 l 862 W 880 W 896 aV	830 l 850 W 852 W 870 aV 894 l	822 l 840 Vl 883 aV 894 l	830 aV 842 aV 859 VW 876 aV 895 Vl	820 aV 839 aV	823 aV 838 l 896 l	830 aV 899 aV	800}l 822} 894 l	808 W 828 l 842 W 858 W 886 W 896 aV	830 l 878 W	822 l 864 aV	826 Vl 852 Vl 894 aV	878 W	811 l	817 Vl 866 aV	805 W 834 Vl	814} 876} aV
912 aV 958 l	904 W 918 W 964 l	920 aV 960 Vl	900 VW 921 W 940 VW 974 Vl	904 aV 972 aV	958 aV	813 l 968 aV	917 aV 973 aV	920 aV 958}l 964}		914 aV	920 aV 946 aV	910 VW 970 aV	918 aV	918 l 935 aV	916} 927} l	928 aV 938 aV	900 aV 970 l
1034 l 1056 W 1062 W	1024 l 1038 W 1056 W 1072 W	1024 Vl 1034 Vl 1062 aV	1035 aV 1052 aV 1072 l	1034 Vl 1064 aV 1077 aV	1005 aV 1031 W	1031 aV 1064 aV	1040 W	1020} 1042} l	1034 aV 1056 W 1062 W	1026 aV 1060 aV	1021 l	1021 l 1030 l 1064 W	1030 aV 1054 W	1024 l	1026 l	1028 l 1031 l 1055 aV	1028 aV
1148 Vl 1169 aV 1196 l	1150 Vl 1172 W	1144 Vl	1120 l 1154 Vl	1153 Vl	1108 aV 1143 l 1194 l	1146 Vl 1194 aV	1154}aV 1165}	1184}l 1190}	1146 aV 1170 l	1141 l 1172 W 1196 W	1159 Vl 1168 aV	1144 Vl	1170 l	1163 l	1109 W 1162 l 1188 Vl	1109 l 1128 W 1160 Vl 1194 W	1142 Vl 1192 aV
1222 W 1262 Vl	1202 W 1220 l 1282 l	1204 Vl 1242 Vl	1288 Vl	1278 Vl	1279 Vl	1262 Vl	1290 Vl	1264}l 1280}	1220 l	1224 W	1212 W l 1231 aV 1292 Vl	1210 W 1252 Vl 1290 Vl	1218 W		1212 W	1263 l	1290 Vl
1330 Vl 1360 l	1348 W	1383 Vl		1344 W	1341 aV 1365 W 1378 l 1398 aV			1370 l	1304 l 1340 W 1384 aV	1312 l 1352 l 1384 aV	1381 Vl	1352 Vl	1382 l		1378 l 1397 aV	1341 aV 1374 aV 1396 aV	1378 aV
1404 aV 1426 Vl 1482 Vl	1408 Vl 1464 Vl	1472 Vl	1468 l	1400 W 1460 Vl	1460 Vl	1424 Vl	1410 VW 1484 aV	1454} 1460} l	1410 l 1454 W 1486 l	1472 l 1486 l 1555 aV	1462 Vl	1466 Vl	1470 Vl	1481 Vl	1462 Vl	1470 Vl	1464 Vl 1514 W
1662 Vl 1678 l			1668 l	1663 Vl	1660 Vl	1651}V 1707} l	1686 l.	1690 Vl	1688 l.	1650} 1670} l	1663 Vl	1644 Vl. 1690 VW	1660} 1686} l	1663 Vl	1668 Vl	1649 Vl	1654 sh
1718 l	1718 Vl	1724 Vl	1716 l.	1716 Vl	1708 Vl		1722 l.	1712 Vl				1722 Vl	1700-l l				1718 Vl

Note: Absorption in the 1380–1460 cm^{-1} region could be due to absorption by the vaseline oil.

Notations: 1. l) intense; w) weak; v l) very intense; v w) very weak; av) average; sh) shoulder. 2. The braces indicate that the bands partially overlap.

TABLE 2

Nos.	Substance	$\nu_{C=O}$ cm^{-1} in solution		$\nu_{C=O}$ cm^{-1} paste in vaseline oil
		CCl_4	$CHCl_3$	
1	$SO_2CH_3FCOOCH_3$	1723	1723	1682—1687, 1717
2	$SO_2FFCOOCH_3$	1730	1722	1718
3	$SO_2ClFCOOCH_3$	1731	1718	1724
4	$CH_3OCFCOOCH_3$	1678, 1722	1676, 1716	1663, 1718
5	$C_4H_9OCFCOOCH_3$	1679, 1718	1676, 1715	1663, 1716
6	$CH_3OOCFCOOCH_3$	1730	1712	1651, 1707
7	$FCOOCH_3$	1730	1712 diffuse	1654, 1704
8	$HOOCFCOOCH_3$	—	1678, 1696—1705 diffuse	1686, 1722
9	$H_2C_4FCOOCH_3$	1704—1712	1696—1704	1696—1712
10	$SO_2FFCOOH$	—	1704	1688
11	NH_2SO_3FCOOH	—	1704	1656
12	$CNFCOOH$	—	1692	1663
13	$CH_3COFCOOH$	—	1663 shoulder 1682	1640, 1718
14	$HOOCFCOOH$	—	—	1660, 1686—1700 diffuse
15	C_2H_5FCOOH	1682	1672	1663
16	C_4H_9FCOOH	1682	1672	1668
17	$FCOOH$		1682	1649
	$CH_3OOCFC_6H_5$	1718	1707	1718

Note. In the case of keto acids and keto esters, the lower frequency is assigned to the ketone carbonyl and the higher to the acid or ester carbonyl. In the case of the monoester and the ester—amide of ferrocenedicarboxylic acid, the higher frequency was assigned to the ester group.

A comparison of the C = O group frequencies of the compounds in chloroform solution shows that the presence of a substituent in the other ring changes the carbonyl group frequency to a significant extent; thus, for esters of ferrocenecarboxylic acid substituents in the second ring gave carbonyl frequencies as indicated: SO_2CH_3, ν_{CO} = 1723 cm^{-1}; C_4H_9 = 1696 - 1704 cm^{-1}; for the substituted acids: SO_2F ν_{CO} = 1704 cm^{-1}, and C_2H_5 and C_4H_9 1672 cm^{-1}. It is also clear from Table 2 that an increase in the electrophilic nature of the substituent increases the frequency of the C = O bond of the carboxyl (and carbomethoxyl) group attached to the other ring of the ferrocene molecule, and, accordingly, the substituents can be arranged in the following orders with respect to effect on carboxyl:

$$C_4H_9 \approx C_2H_5 < COOCH_3 < COCH_3 < CN < SO_2NH_2 \approx SO_2F, \qquad (2)$$

with respect to effect on carbomethoxyl:

$$C_4H_9 < C_2H_5 < COOH < COOCH_3 < COC_6H_5 \approx COCH_3 < SO_2Cl < SO_2F \approx SO_2CH_3. \qquad (3)$$

These series are in good agreement with each other and with the series based on a comparison of the dissociation constants of ferrocenecarboxylic acids. An exception is the position of the absorption bands of unsubstituted acids and esters which are found at 1712 cm^{-1} for the ester and at 1682 cm^{-1} for the acid; i.e., hydrogen falls in the series between the CH_3CO and CH_3OOC groups, while in the series based on acid dissociation constants, hydrogen falls between the alkyl and $COOCH_3$ groups. We still do not have an explanation for this.

In spite of this discrepancy, the infrared spectra confirm the conclusion that the effect of substituents is transmitted from one ring of the ferrocene molecule to the other, and the effect of substituents on the carbonyl frequency of the carboxyl (or, correspondingly, carbomethoxyl) group has basically the same character as the effect on dissociation of the carboxyl group; i.e., an increase in the characteristic frequency of the C=O bond occurs concurrently with an increase in the dissociation constant of the corresponding acid.

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THE INTERACTION OF φ-OLEFINS [PERFLUOROOLEFINS] WITH HYDROXYLAMINE

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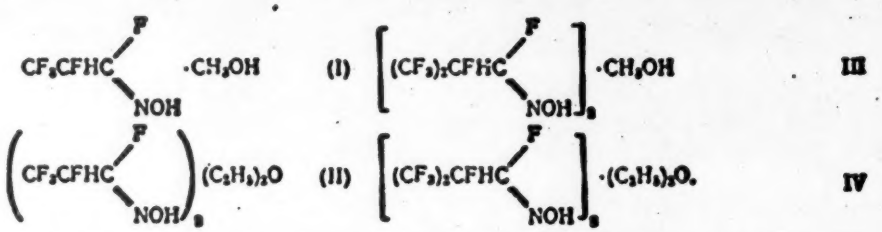
Among the numerous addition reactions of nucleophilic reagents to perfluoroolefins, the addition of hydroxylamine has not been studied. As would be expected, hydroxylamine adds readily to perfluoropropylene and perfluoroisobutylene; the exothermic reaction begins readily when perfluoropropylene (or perfluoroisobutylene) is passed into an alcohol (or ether) solution of hydroxylamine precooled to a low temperature (0° in the case of perfluoropropylene and -50° in the case of perfluoroisobutylene). The initially formed products of the addition of hydroxylamine to the perfluoroolefin are unstable and spontaneously split out hydrogen fluoride during the course of the reaction, being converted thereby to hydroxamic acid fluorides of the corresponding 2-monohydroperfluorocarboxylic acids. The hydrogen fluoride liberated combines with the hydroxylamine

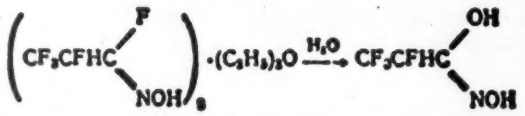
$$CF_3CF=CF_2 + NH_2OH \rightarrow [CF_3CFHCF_2NHOH] \xrightarrow{-HF} CF_3CFHC(F)=NOH$$
$$HF + NH_2OH \rightarrow NH_2OH\cdot HF.$$

The resulting 2-hydroperfluoropropionohydroxamic and 2-hydroperfluoroisobutyrohydroxamic acid fluorides were isolated in the form of complexes with the alcohol or ether (depending on the solvent used).

These compounds were colorless, transparent liquids with a sharp odor; they were insoluble in water and readily soluble in the usual organic solvents. They gave a positive test for hydroxamic acids with ferric chloride in a boiling aqueous solution of sodium bicarbonate. The structures of these compounds were proved by the following transformations.

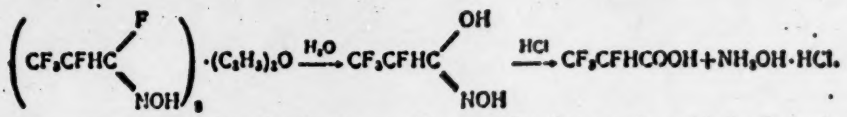


1. The complex of 2-hydroperfluoropropionohydroxamoyl fluoride with ether was hydrolyzed with water, hydrochloric acid (d = 1.19), and sulfuric acid (d = 1.84). In the first case, the previously undescribed 2-hydroperfluoropropionohydroxamic acid was obtained in 25 % yield; the colorless crystals melted at 98-99°.

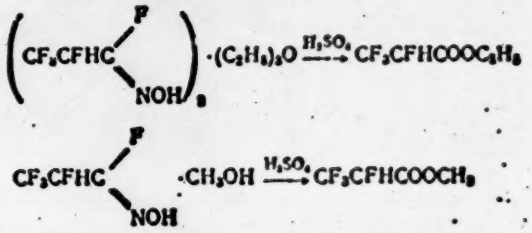


This same acid was obtained from the methyl ester of 2-hydroperfluoropropionic acid and hydroxylamine. A mixture of the hydroxamic acids prepared by these two methods showed no depression of the melting point.

The hydrolysis with concentrated hydrochloric acid led to the formation of 2-hydroperfluoropropionic acid (identified as the amide).

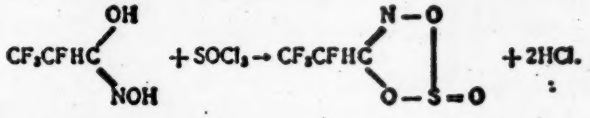


The action of concentrated H_2SO_4 brought about a peculiar esterification reaction with the formation of esters of 2-hydroperfluoropropionic acid. The physical constants of the methyl and ethyl esters and of the amide prepared from them were in agreement with those reported previously [1].

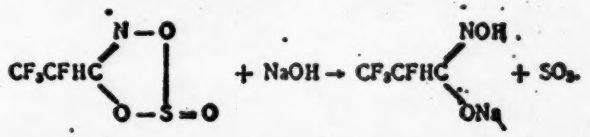


2. The reaction between the ether complex of 2-hydroperfluoropropionohydroxamic acid and an alcoholic solution of sodium methylate resulted in the formation of the methyl ester of 2-hydroperfluoropropionic acid and sodium fluoride; this confirms the presence in the compound of an acid halide fluorine. Hydrolysis with concentrated HCl of the ether and alcohol complexes of the acid fluorides of 2-hydroperfluoroisobutyrohydroxamic acid gave good yields of 2-hydroperfluoroisobutyrohydroxamic acid, $(CF_3)_2CHC(OH)NOH$ (m.p. 119.5-120°). These complexes differ with respect to stability. Thus, if the reaction mixture resulting from the passage of perfluoropropylene through an alcoholic solution of hydroxylamine is immediately distilled, the complex of 2-hydroperfluoropropionyl fluoride with alcohol is separated. If the same reaction mixture is diluted with ether before distillation, the major reaction product is a complex of the acid fluoride with ether; thus, the alcohol is replaced by ether.

The hydroxamic acids can easily be distilled under vacuum; when heated with thionyl chloride, they lose two molecules of hydrogen chloride and form cyclic compounds:



Under the influence of a base, these cyclic compounds lose sulfur dioxide and yield a salt of the hydroxamic acid



EXPERIMENTAL PART

1) The interaction of hydroxylamine with perfluoropropylene. a) Into a 4-necked flask, fitted with a stirrer, a thermometer, a gas supply tube, and a gas effluent tube, was placed 33 g (1 mole) of a freshly prepared solution of hydroxylamine in 250 ml of methanol, and perfluoropropylene was passed into the stirred, ice-cooled mixture. The precipitated hydroxylamine hydrofluoride was filtered, and the filtrate was distilled under reduced pressure. The alcohol complex of α-monohydroperfluoropropionohydroxamoyl fluoride (I) was a colorless liquid with a sharp, disagreeable odor. Its b.p. was 37.5-38.5° per 50 mm. The yield was 48 % (based on the perfluoropropylene); d_4^{22} 1.3820; n_D^{22} 1.3294; MR_D found 28.70; MR_D calc. 28.76.

Found %: C 23.97; N 7.14; F 48.01 $CF_3CFHC(=NOH)\cdot CH_3OH$. Calculated %: C 24.63; N 7.19; F 48.70

2 labile hydrogen atoms were found in the compound.

b) Perfluoropropylene was bubbled into a suspension of 14 g of free hydroxylamine in 100 ml of dry ether while the suspension was stirred and cooled with ice. The precipitated hydroxylamine hydrofluoride was filtered, and the filtrate was distilled under reduced pressure. The resulting α-monohydroperfluoropropionohydroxamoyl fluoride complex with ether was a sharply reeking, colorless liquid. The b.p. was 34-35° per 50 mm. The yield was 57 %. d_4^{22} 1.3415; n_D^{22} 1.3335; MR_D found 30.64; MR_D calc. 31.56.

Found %: C 29.90; N 7.25; F 46.90 $[CF_3CFHC(=NOH)]_2(C_2H_5)_2O$. Calculated %: C 30.00; N 7.04; F 47.50

One labile hydrogen atom was found in the compound.

2) 5 g of acid fluoride (II) and 30 ml of water were heated, with stirring, on a boiling water bath. Evaporation of the reaction mixture under vacuum gave white, lammelar crystals. M.p. 98-99° (from chloroform). The crystals were readily soluble in water and alcohol and sparingly soluble in ether and chloroform. With ferric chloride, an aqueous solution of the crystals gave the red color characteristic of hydroxamic acids.

Found %: N 8.69; F 46.72. $CF_3CFHC(OH)=NOH$. Calculated %: N 8.63; F 47.20

3) 8 g of acid fluoride (II) was heated for a period of two hours at 100° with 15 ml of concentrated HCl. The resulting solution was extracted with ether, and the ether extract was washed with sodium bicarbonate solution and with water and dried with calcium chloride. After distillation of the ether, the residue distilled at 135-137° d_4^{22} 1.4590; n_D^{22} 1.3275. The molecular weight was determined by titration with a base; found 163.5, calculated 164.

Found %: F 46.50. $CF_3CFHCOOH\cdot H_2O$. Calculated %: F 46.34

A mixture of the amide prepared from this acid with α-monohydroperfluoropreplonamide prepared by another route showed no depression of the melting point.

4) 28 g of concentrated H_2SO_4 and 1 g of ground glass were placed in a round-bottom flask fitted with a reflux condenser and a dropping funnel, and 21 g of acid fluoride (II) was carefully added from the dropping funnel. The mixture was heated for 20 minutes on a boiling water bath. The mixture was distilled, and a fraction boiling at 105-120° per 745 mm was collected. This fraction was washed with water, and a second distillation gave 12 g of a colorless, transparent liquid with a pleasant* odor; it did not contain nitrogen. B.p. 106-107°. d_4^{22} 1.2850; n_D^{22} 1.3268. The constants of this compound were in good agreement with the literature values for the ethyl ester of α-monohydroperfluoropropionic acid; the action of ammonia gave the amide with an m.p. of 57-58°, and a mixture of the amide with a specially prepared sample showed no depression of the melting point.

5) 14.5 g of acid fluoride (I) and 20 g of concentrated H_2SO_4 were placed in a round-bottom flask fitted with a reflux condenser. The mixture was heated on a boiling water bath for 20 minutes. The reaction mixture was then distilled, and 10.5 g of a colorless liquid boiling at 99-100° was collected. The liquid was washed with water, and a second distillation gave a fraction boiling at 93-95°. d_4^{17} 1.3950; n_D^{17} 1.3212. The constants of this substance were close to those of the methyl ester of α-monohydroperfluoropropionic acid. Reaction with ammonia gave the amide, and a mixture of this amide with a specially prepared sample of α-monohydroperfluoropropionamide showed no depression of the melting point.

6) The interaction of hydroxylamine and perfluoroisobutylene. a) The alcohol complex of α-monohydroperfluoroisobutyrohydroxamoyl fluoride (III) was prepared in a manner analogous to the preparation of (I). Acid fluoride (III) was a colorless, transparent liquid with a disagreeable odor. B.p. 44-44.5° per 80 mm, 105.5-106.5° per 750 mm. d_4^{22} 1.5560; n_D^{22} 1.3190; MR found 29.10, $MR_{calc.}$ 30.09.

Found %: C 22.88; H 1.26; N 6.42; F 58.50 $[(CF_3)_2CHC(=NOH)]_2\cdot CH_3OH$. Calculated %: C 23.55; H 1.14; N 6.11; F 58.10.

* As in the original Russian.

b) The ether complex of α-monohydroperfluoroisobutyrohydroxamoyl fluoride (IV) was prepared in a manner analogous to that used in the preparation of acid fluoride (II). Acid fluoride (IV) was a colorless, sharply reeking liquid, b.p. 113-114° per 745 mm. The yield was 58%. d_4^{19} 1.4170; n_D^{19} 1.3261; MR_{found} 35.60; $MR_{calc.}$ 36.1

Found %: F 53.35. $[(CF_3)_2CHC = NOH]_2 \cdot (C_2H_5)_2O$. Calculated %: F 53.20.

7) Heating acid fluoride (III) with concentrated HCl (the experiment was carried out similarly to Experiment No. 3) gave α-monohydroperfluoroisobutyrohydroxamic acid. The colorless crystals, which were readily soluble in water, gave a positive reaction with ferric chloride for hydroxamic acid. After vacuum distillation, the substance melted at 119.5-120°.

Found %: N 6.83; F 53.31 $(CF_3)_2CHC = NOH$. Calculated %: N 6.63; F 54.01

8) 20 ml of dry ether, 10 g of acid fluoride (II), and several drops of phenolphthalein were placed in a flask fitted with a reflux condenser and a dropping funnel. A solution of sodium methylate in methanol was added from the dropping funnel until a rose color appeared. The reaction mixture was distilled under vacuum. After distillation of the ether and alcohol, a substance distilled which, according to its constants, was the methyl ester of α-monohydroperfluoropropionic acid. B.p. 94-95° per 740 mm; d_4^{22} 1.3340; n_D^{22} 1.3207.

This ester was converted to the amide, and a mixture of this amide with a specially prepared sample of α-monohydroperfluoropropionamide showed no depression of the melting point.

9) 4 g of α-monohydroperfluoropropionohydroxamic acid and 12 ml of dry benzene were placed in a flask fitted with a reflux condenser. The mixture was heated on a boiling water bath, and 3.2 g of thionyl chloride was added dropwise. Hydrogen chloride was evolved. After distillation of the benzene, a colorless, sharply reeking liquid distilled; b.p. 56-56.5° per 57 mm, d_4^{22} 1.6656; n_D^{22} 1.3737.

Found %: C 17.12; H 0.30; N 6.68; F 37.14; S 15.51 $C_3HF_4O_3NS$. Calculated %: C 17.36; H 0.48; N 6.76; F 36.75; S 15.45.

10) The reaction was carried out as in the preceding experiment. From 4 g of α-monohydroperfluoroisobutyrohydroxamic acid was obtained 2.3 g of a colorless liquid with a b.p. of 55° per 40 mm, d_4^{22} 1.6710; n_D^{22} 1.3580.

Found %: C 44.45; N 6.02; S 12.40 $C_4HF_6O_3NS$. Calculated %: C 44.30; N 5.45; S 12.45.

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CATALYTIC TRANSFORMATIONS OF ALKYLCYCLOPROPANES IN THE PRESENCE OF PLATINUM AND PALLADIUM SUPPORTED ON ASHLESS ACTIVATED CARBON

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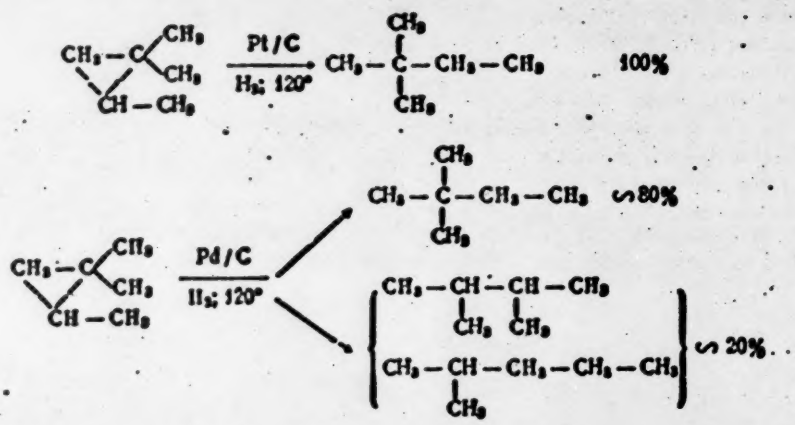
We recently showed that the hydrogenation of alkylcyclopropanes in the presence of platinized carbon proceeds differently than in the presence of palladinized carbon [1]



In the presence of the first catalyst and at temperatures of 120° and 220°, only hydrogenolysis of the three-membered ring occurs, while in the presence of the palladium catalyst, isomerization of the alkylcyclopropane to an olefin with subsequent addition of hydrogen takes place in addition to the hydrogenolysis reaction. With an increase in the temperature to 220° the amount of by-products in the catalyzate increases to 40%.

It is possible that this side reaction is due to the palladium, provided that, in contradistinction to platinum, it is capable of causing isomerization of the three-membered ring, or it may be due to the carrier (carbon) which as we have shown [2], is not inert in this reaction. If the latter possibility is correct, it is not clear why this property of carbon appears in the case of the palladium catalyst and does not appear in the case of the platinum catalyst, nor is it clear whether this is a consequence of the lower activity of the palladium catalyst in the hydrogenolysis reaction, as we previously proposed [1].

Thus, the problem comes down to one of investigating and comparing the properties of the metals themselves, platinum and palladium, under alkylcyclopropane isomerization and hydrogenolysis conditions while excluding the effect of the support. For this purpose, it would have been simplest to use the metals in the form of blacks. It developed, however, that the surface of these blacks was so small that either a very large amount of the metal or considerably more vigorous reaction conditions were required.

Thus, neither platinum nor palladium black causes any hydrogenolysis of alkycyclopropanes at 120°. Hence,

TABLE 1

Hydrocarbon	B.p., deg C(769 mm)	n_D^{20}	d_4^{20}	Aniline point, deg C
Ethylcyclopropane	35,0	1,3786	0,6841	17,9
1,1,2-Trimethylcyclopropane	52,6	1,3862	0,6948	48,3
2-Methylpentane [5]	60,27	1,3714	0,65315	74,6
2,2-Dimethylbutane[5]	49,7	1,3687	0,64916	81,2
2,3-Dimethylbutane[5]	57,9	1,37495	0,66161	71,9

Fig. 1. a) Catalyzate from 1, 1, 2-trimethylcyclopropane over platinized carbon; b) catalyzate from 1, 1,-2-trimethylcyclopropane over palladinized carbon.

it was necessary to select a support with sufficient surface but inert with respect to isomerization of the three-membered rings.

Silica gel, aluminosilicate, kieselguhr, and pumice are unsuitable for this purpose, since all of these substances, like activated carbon, are capable of isomerizing the three-membered ring [3].

Activated ashless carbon, which we prepared by carbonizing sugar, proved to be inert in the temperature range of up to 220°. Its surface (240 sq m/g) was less than the surface of the activated carbon which we had used in all of our preceding work (480-540 sq m/g), but, as the experiments showed, it was sufficient for a comparison of the properties of the metals deposited on it. When alkylcyclopropanes were passed through this carbon at 220°, they underwent no change.

Using this carbon as a base, platinum and palladium catalysts containing 20% metal were prepared. The experiments in the absence of hydrogen (isomerization) were carried out at a temperature of 220°, which appeared to be optimum from our previous work [1,2,3]. It was found that the properties of the alkylcyclopropanes had not changed after contact with either catalyst and that the catalyzate contained no unsaturates. It thus appeared that neither platinum nor palladium causes isomerization of the three-membered ring under these conditions.

The experiments in the presence of hydrogen were carried out with 1,1,2-trimethylcyclopropane at a temperature of 120°, at which temperature hydrogenation over these catalysts was incomplete, so that a comparison of their activities was possible. It was found that isomerization did not occur; hydrogenolysis proceeded to the extent of 65% in the case of the platinum catalyst and 50% in the case of the palladium catalyst; this indicates that the palladium catalyst has lower activity with respect to hydrogenolysis of the three-membered ring.

Turning now to the catalysts mentioned at the beginning of the article, we may consider it proved that the isomerization which takes place over the palladinized carbon is caused not by the metal but by the support; the difference in the action of the two catalysts under hydrogenation conditions depends on the relative activities of platinum and palladium as hydrogenolysis catalysts. In the case of the more active metal, the rate of the hydrogenolysis reaction so far exceeds the rate of isomerization, which is caused by the support, that the effect of the support is not apparent at all. In the case of the less-active metal, the rates of the two reactions are competitive, and the side reaction caused by the support proceeds along with hydrogenolysis.

EXPERIMENTAL PART

Catalysts. The platinum and palladium blacks were prepared by the method of Zelinskii [4].

Ashless carbon. The sugar was recrystallized three times from alcohol, dried, and carbonized in small portion in a porcelain crucible in a muffle furnace at 800-900°. Activation of the carbon was carried out in a stream of carbon dioxide at 600° in a rotating quartz tube heated by a circular muffle furnace. The ash was 0,05%, and the surface (determined iodometrically) was 240 sq m/g.

Platinized and palladinized carbon (20%) were prepared by deposition of the metals on the ashless carbon using the method of Zelinskii [4]; 10 ml of catalyst contained about 0,6 g of Pt or Pd.

The experiments were carried out under the conditions described previously [1,2,3]. The hydrocarbon space rate was 0,2 hours^{-1} in all cases. The properties of the alkylcyclopropanes used in the present work and also the

TABLE 2

Hydrocarbon	Catalyst	Properties of catalyzate		
		Unsaturates content	n_D^{20}	d_4^{20}
1,1,2-Trimethylcyclopropane	Pt-black*	None	1,3862	0,6948
Same	Pd-black	None	1,3862	0,6950
Ethylcyclopropane	Ashless carbon	Traces	1,3789	0,6840
1,1,2-Trimethylcyclopropane	" "	None	1,3864	0,6950
Same	Pt/ ashless carbon	None	1,3864	0,6951
" "	Pd/ ashless carbon	Traces	1,3862	0,6948

* The blacks, in an amount of 2.7 g, were deposited on glass wool, which was used in an amount such that the catalyst occupied a volume of approximately 10 ml. The remainder of the catalysts were used in 10 ml amounts (about 3 g).

TABLE 3

Fraction No.	Amount, g	B.p., °C (170 mm)	n_D^{20}	d_4^{20}	Aniline point, °C
With platinized carbon					
1	1,7	49,4—49,7	1,3692	0,6515	78,2
2	5,9	49,7—51,2	1,3722	0,6585	73,2
3	1,8	51,2—52,5	1,3819	0,6836	58,5
4	1,7	52,5—56,3	1,3830	0,6850	54,0
Loss	0,7				
With palladinized carbon					
1	3,7	48,5—49,4	1,3700	0,6625	74,0
2	1,6	49,4—50,4	1,3740	0,6617	71,0
3	2,4	50,4—51,6	1,3821	0,6843	55,7
4	2,9	51,6—55,4	1,3828	0,6844	55,0
Loss	0,3				

properties of the paraffins which could be formed during hydrogenation of 1,1,2-trimethylcyclopropane are presented in Table 1. Data from the experiments studying the behavior of alkylcyclopropanes over the different catalysts in the absence of hydrogen (in a stream of nitrogen) at a temperature of 220° are presented in Table 2.

The data presented in Table 2 show that none of the catalysts investigated cause any appreciable amount of isomerization of alkylcyclopropanes. The catalyzates obtained with platinized and palladinized ashless blacks were distilled in a column having an efficiency of 40 theoretical plates; 10 ml of n-heptane (n_D^{20} 1,3876; d_4^{20} 0,6835) was used as a chaser. Distillation data are presented in Table 3 for the catalyzate from the experiment in which 1,1,2-trimethylcyclopropane was passed over platinized carbon, and similar data are presented in Table 3 and in Figure 1 for the catalyzate from the experiment using palladinized carbon.

A comparison of the data presented in Table 3 with the hydrocarbon properties presented in Table 1 shows that in both cases the catalyzate was a mixture of unreacted 1,1,2-trimethylcyclopropane and 2,2-dimethylbutane. The increase in aniline point with an increase in the boiling range of the fractions indicates that neither 2,3-dimethylbutane nor 2-methylpentane was present in the catalyzate. Calculation of the compositions of the binary mixtures on the basis of additivity of refractive index, specific volume, and aniline point shows that there was 65% hydrogenolysis in the case of platinized carbon and 50% in the case of palladinized carbon.

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SEPARATION AND PROPERTIES OF HIGHER α,α,α,ω-TETRACHLOROALKANES

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Telomerization of ethylene with carbon tetrachloride forms a mixture of telomers, of which the α,α,α,ω-tetrachloroalkanes containing up to 15 carbon atoms have been separated and described [1,2,3].

We have studied conditions for vacuum fractionation of higher tetrachloroalkanes in a Vigreux column at pressures of 0.2-0.5 mm, and we have been able to separate in the pure state telomers containing up to 23 carbon atoms in the molecule.

A column with "star"-type indentations [4] but of somewhat modified construction was used for the fractionations. The column, which had a height of 30 cm and an interval diameter of 14-16 mm, had a total throughput below the flood point (at total reflux) of 100-200 ml/hour or 60-100 drops/minute. The fractionating efficiency of the column, which was determined with a toluene-heptane mixture, was 4-5 theoretical plates. The fractionation was carried out with continuous takeoff at reflux ratios of 6-8 for tetrachlorotridecane and higher telomers.

The column resistance was negligible, which permitted us to carry out the distillation with the temperature of the liquid in flask 25-35° higher than the vapor temperature during fractionation of multicomponent mixtures

TABLE 1

Constants of Higher Tetrachloroalkanes, $Cl(CH_2)_nCCl_3$

Tetrachloroalkane	B.p.,* deg C at 0.30 mm Hg	d_4^{20}	Vis. at 20°, centistokes	n_D^{20}	MR found	MR calc.	Found, % C	Found, % H	Found, % Cl	Calculated, % C	Calculated, % H	Calculated, % Cl
C_{10}	130	1,1166	14,61	1,4801	81,24	81,69						
C_{11}	149	1,0935	19,65	1,4795	90,94	90,93						
C_{12}	166	1,0773	21,89	1,4795	99,63	100,17	53,78 53,89	8,31 8,18		53,08	8,53	
C_{13}	181	1,0546	29,30	1,4795	109,30	109,41	56,24 56,04	8,73 8,69	34,85 35,20	56,14	8,93	34,90
C_{14}	194	1,0361	35,51	1,4790	118,89	118,65	58,05 57,92	9,22 9,11	32,42 32,35	58,06	9,28	32,65
C_{15}	207	1,0192	42,10	1,4784	128,44	127,88	59,84 59,83	9,18 9,30	30,61 30,54	59,74	9,59	30,67

* Average boiling point at a pressure of 0.25-0.35 mm Hg with variations of ± 2-6° in different experiments.

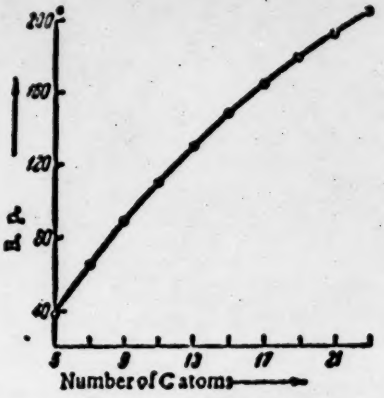

Fig. 1. Relationship between boiling points of the tetrachloroalkanes at 0.25–0.35 mm and molecular weight.

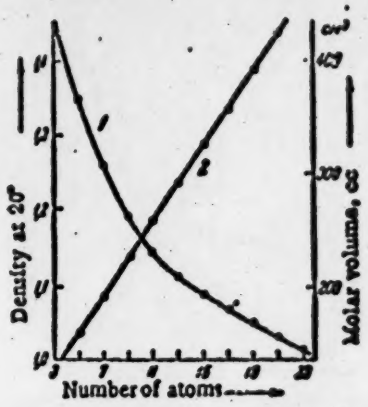

Fig. 2. Density (1) and molar volume (2) of tetrachloroalkanes as functions of molecular weight.

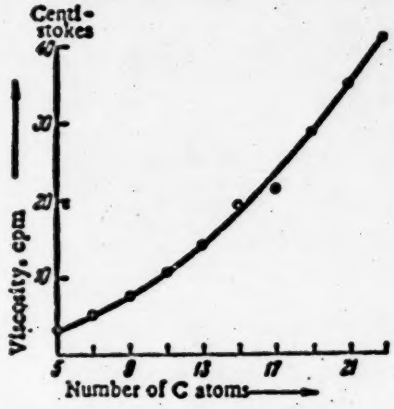

Fig. 3. Viscosity of tetrachloroalkanes.

TABLE 2

Higher ω-Chlorocarboxylic Acids

Tetrachloroalkane	Hydrol. w. H_2SO_4: yield, % of theor.	Hydrol. w. H_2SO_4: m.p., °C	Hydrol. w. HNO_3: yield, % of theor.	Hydrol. w. HNO_3: m.p., °C
C_{11}	74	39	77	38
C_{13}	65	51	47	49—51
C_{15}	58	—	63	54—58
C_{19}	—	—	51	58
C_{21}	—	—	38	62

and 10–15° higher during redistillation of narrow fractions.

The tetrachloroalkanes were separated from a mixture of telomers produced in equipment of the Kaluzhkii Combine of Synthetic and Natural Perfumes [5] at a pressure of 150 atm and a mole ratio of ethylene to carbon tetrachloride of about 20:1. The mixture contained about

30% $C_5 + C_7$, 30% $C_9 + C_{11}$, 12% $C_{13} + C_{15}$ and 28% $C^*_{>15}$.

A technical mixture of telomers prepared in steel reactors always contains traces of metal chlorides which accelerate dehydrochlorination of the tetrachloroalkanes [6], especially at temperatures above 160°. We found that the addition of up to 5% soda ash during the distillation converts the metal chlorides to less-active basic salts, thereby very sharply decreasing the rate of catalytic decomposition of the tetrachloroalkanes. However, the separation of telomers above C_{15} by rectification of the technical mixture was difficult even with the addition of soda.

Therefore, making use of the different solubilities of tetrachloroalkanes in organic solvents [2], we extracted (after distillation of the C_5–C_9 fraction) broad fractions containing telomers up to C_{17} and C_{25}, respectively, using ethyl alcohol and acetone as the solvents. These fractions, which were free from insoluble waxy telomers and impurities, distilled with less decomposition. These broad fractions were rapidly distilled from a flask at a pressure of 0.1–0.3 mm Hg, narrower fractions containing 3–4 components were collected, and these were fractionated.

In order to obtain the individual telomers described in Table 1 the substances separated during the first fractionation were distilled a second time in the same column.

The regular change in boiling point for the entire series of tetrachloroalkanes from C_5 to C_{23} is shown in

* The α,α,α,ω-tetrachloroalkanes here and in the remainder of the article are indicated by the number of carbon atoms in the molecule, e.g., C_5, C_7, etc.

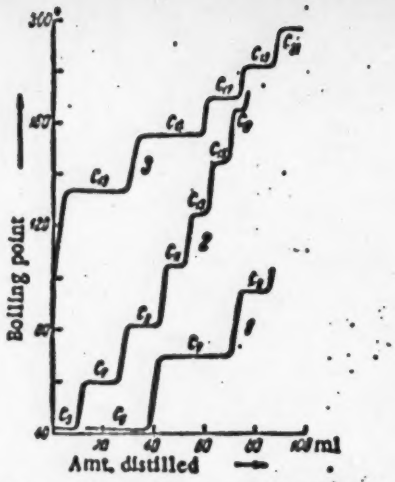

Fig. 4. Distillation curves for mixtures of tetrachloroalkanes; 0.2-0.5 mm pressure: 1 and 2) original mixtures obtained by telomerization reaction at 150 atm, 1) 4 moles ethylene per mole CCl_4; 2) 10 moles ethylene per mole CCl_4; 3) broad fraction of higher telomers separated with acetone from the reaction mixture (150 atm, 20 moles ethylene per mole CCl_4).

Figure 1. The point for C_3 was obtained by extrapolation of the linear graph of $\lg P = f\left(\frac{1}{T}\right)$, plotted using points for P = 2-100 mm (T is absolute boiling point).

Figure 2 shows graphically the variation in density and in molar volume with the molecular weight of the tetrachloroalkane.

The molar volumes of mixtures of tetrachloroalkanes are additive, as we showed unequivocally, using synthetic mixtures and mixtures of tetrachloroalkanes obtained by telomerization reactions.

Viscosities of tetrachloroalkanes have previously been determined only for the lower telomers [7]. We determined the viscosities at 20° of the entire series of tetrachloroalkanes using an Ostwald-Pinkevich viscosimeter for this purpose. The results are presented in Table 1 and Figure 3*.

The tetrachloroalkanes used for the determinations of physical constants were narrow fractions collected within a range of 1-2° during distillation of the mixtures and broad fractions (see Figure 4 for distillation curves) and redistilled in the same column**. Proof of the purity of the substances investigated is that during a check distillation, they completely distilled within 1° and their constants were not changed.

The corresponding ω-chlorocarboxylic acids, with the properties shown in Table 2, were prepared from the C_{11} to C_{21} tetrachloroalkanes by hydrolysis with sulfuric or nitric acid under conditions previously described in references [3] and [8].

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* The determinations were made by L. M. Shulov.

** The distillations were carried out by Yu. P. Chizhov.

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CONTRIBUTION TO THE PROBLEM OF THE INTERACTION OF PHENYL RADICALS WITH BENZENE

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In free-radical reactions in the liquid phase, the interaction of the radicals formed by dissociation (by temperature, light, etc.) of the initial compound (R:R) with the solvent — medium (X:S) is of very great significance. In spite of its importance, studies of this problem have only very recently been initiated.

In the first place, the initial material can form with the solvent an intermediate complex [R:RX:S], which then homolytically decomposes to RX and RS without the formation of radicals in the free state. In the second place, the substance can become solvated, and, during its decomposition into radicals, the latter can react with each other in a "cage" without escaping into the volume of the solvent. Finally, the radicals can be forced out of the "cage" into the volume of the solvent, forming with the solvent the intermediate complex [R·X:S]. In this case, the radicals can bring about chain processes. Radical transfer can occur through an exchange of a radical R, for a peripheral atom, X, of the solvent:

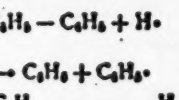
$$R\cdot + X:S \rightarrow R:X + S\cdot.$$

The system in which R = S is a special case. In this case, the radical is regenerated, and its kinetic lifetime is lengthened.

In the present work, we investigated the interaction of phenyl radicals with benzene, using a number of compounds which decompose homopolarly with the formation of a phenyl radical. In order to be able to detect radical-transfer reactions, it was necessary to use compounds labeled with tagged atoms. We used for this purpose radiocarbon C^{14}, which was introduced both into the initial compound and into the benzene; i.e., two systems were studied: labeled dissociating compound + inactive benzene and unlabeled compound + active benzene. The following three routes for the interaction of a phenyl radical with benzene (I) may be assumed:

$$C_6H_5\cdot + C_6H_6 \rightarrow C_6H_5 - C_6H_5 + H\cdot \qquad (I)$$

$$C_6H_5\cdot + C_6H_6 \rightarrow C_6H_6 + C_6H_5\cdot \qquad (II)$$

$C_6H_5\cdot + C_6H_6 \rightarrow$  (III)

Reaction (I) is improbable from thermodynamic considerations; (II) is probable, but has not been experimentally confirmed; (III) has been assumed by many authors [2], and has recently received experimental confirmation [3]. However, the occurrence of process (III) does not exclude reaction (II). It is quite probable that the first act of the interaction is the formation of the π-complex (IV), which can undergo transition to σ-complex (III) or which can undergo an internal radical transfer:

TABLE 1

Expt. No.	Taken for the reaction: Substance decomposing into radicals: compound	g	activity, imp/min	total activity imp/min	Benzene: g	mole ratio	activity	Reaction conditions: Irradiation, heating	Added substance	Temperature, °C	Time, hours	Obtained: Biphenyl: activity, imp/min	% phenyl groups from benzene	Benzene: activity, imp/min	total activity imp/min	% benzene from decomposing subs.	Note: Activity of subs. formed by the reaction, imp/min
1	DPM*	3,0	—	—	27,0	40	663	*hν*	—	40	100	159	24,0	—	—	—	DMP* — 47
2	DPM*	0,7	7573	$2,4 \cdot 10^6$	3,9	25,0	—	*hν*	—	40	30	4660	38,5	48	$1,9 \cdot 10^5$	7,9	
3	DPM*	0,9	—	—	16,0	90	2900	Heat	Catal. Pt	170	17	30	1,0	—	—	—	
4	DPM*	2,0	—	—	18,0	45	725	Heat	Catal. Cu	170	70	12	1,6	—	—	—	
5	BP	60,0	—	—	221,0	11,5	925	Heat	—	80	21	364	39,0	825	—	—	
6	BP	1,0	7280	$3,9 \cdot 10^6$	3,5	10,0	—	Heat	—	80	8	5250	36,8	119	$3,0 \cdot 10^5$	9,3	
7	BP	1,5	—	—	158	300	1450	Heat	$Hg(OAc)_2$	80	8	680	47,0	—	—	—	C_6H_5HgCl — 170
8	BP	2,4	—	—	128	150	1390	Heat	$Hg(OAc)_2$	80	8	647	47,0	—	—	—	C_6H_5HgCl — 86
9	BP	1,7	—	—	10,3	18	1500	*hν*	—	40	167	140	9,3	—	—	—	
10	BP	1,7	3190	$3,6 \cdot 10^6$	10,3	20	—	*hν*	—	40	270	3200	10,0	6	$4,3 \cdot 10^4$	1,2	
11	LTB	3,0	—	—	14,5	50	1512	Heat	—	80	8	748	49,0	—	—	—	
12	LTB	3,4	17000	$2,2 \cdot 10^7$	6,0	16	—	Heat	—	80	8	7775	54,3	1	$4,9 \cdot 10^5$	0,1	
13	NAA	3,0	—	—	7,8	5	825	Heat	—	40	0,5	412	50,0	—	—	—	
14	NAA	1,5	2000	$1,4 \cdot 10^6$	3,8	5	—	Heat	—	40	0,5	1520	47,2	7	$1,9 \cdot 10^4$	1,4	

* DPM = diphenylmercury; BP = benzoyl peroxide; LTB = lead tetrabenzoate; NAA = nitrosoacetanilide.

Notes. 1) BP and NAA containing radiocarbon in the benzene rings were used in Experiments 6 and 14. 2) LTB labeled with C^{14} in all positions was used in Experiment 12. 3) In experiments 2, 6, 10, 11, and 14, the percent phenyl groups from benzene was calculated by deducting from one hundred per cent the percentage found from the activity. 4) The radiometric analysis of the starting materials and reaction products was carried out by burning the substances and measuring the activity of the resulting carbon dioxide with an internal gas-flow counter. The error in the measurements was 3%; the activity is expressed in imp./minute.

We were able to show the occurrence of process (II) in two cases. This was first shown for the case of the decomposition of diphenylmercury (DPM) in deuterated benzene [4], and was later confirmed in C^{14}-labeled benzene [5]. We have once more confirmed this reaction by experiments in which the components were heated or the reaction mixture irradiated. From the results obtained both with labeled DPM and with labeled solvent — benzene, it is clearly evident that in the photoreaction (Table 1, Experiments 1 and 2), the biphenyl was formed mainly from phenyl groups from the DPM, but it was also partly formed from phenyl groups from the benzene. In turn, part of the phenyl groups from the DPM were converted to benzene. These conversions are most simply explained by the occurrence of process (II). Very weighty evidence of this assumption is the formation of active DPM through the interaction of π-complex (IV) with metallic mercury in experiments in which DPM was decomposed in active benzene. It is well known that the thermal decomposition of DPM, like that of other organometal compounds, is strongly catalyzed by finely divided metals [6]. It may be assumed that such decomposition proceeds on the surface of the metal. We carried out experiments on the decomposition of DPM in benzene with the addition of Pt (Experiment 3) and Cu (Experiment 4). In this case, biphenyl was formed only at the expense of the DPM. Labeled phenyl radicals dimerized on the surface of the metal, and did not transfer into the volume of the solution.

Benzoyl peroxide (BP) was used as another source of phenyl radicals. The reaction of BP with benzene is, as is well known, a more complex reaction which results in the formation of a mixture of many products. The major product of the reaction, biphenyl, is formed from phenyl radicals from the benzoyl peroxide. It is evident from the experimental data (Experiment 5) that radicals from BP predominate in the biphenyl. This was also noted earlier with deuterated compounds [2]. However, here too it was completely evident from experiments with C^{14} in the nucleus of the BP that part of the phenyl radicals transfer into the volume of the solution in the form of benzoyl radicals (Experiment 6) through reaction (II). For more conclusive proof of this process, we used the initiated decomposition of mercuric acetate [7]. This reaction was initiated by BP in a medium of labeled benzene (Experiments 7 and 8). Phenylmercury chloride, which was separated from the products of the reaction by treatment of the phenylmercury acetate formed in the reaction, contained a very significant amount of phenyl radicals from the benzene. Moreover, the following circumstance was noted in the reaction of BP with benzene. It is known from the work of Gelissen and Hermans [8] that besides biphenyl, small amounts of other, more phenylated compounds of benzene, terphenyl, and quaterphenyl, are also obtained in this reaction. It has been proposed that they are products of the successive phenylation of biphenyl. However, there is a certain conspicuous nonconformity in the isotope composition of the biphenyl and quaterphenyl. The isotope composition of the latter compound corresponded to two benzene nuclei from BP and two from benzene, while phenyl radical somewhat predominated in the biphenyl. Therefore, it could be assumed that the quaterphenyl was obtained from biphenyl by subsequent phenylation. It was possible to verify this experimentally. Labeled biphenyl was introduced into the reaction mixture. The quaterphenyl obtained as a result of this reaction was completely inactive. The mechanism of the formation of quaterphenyl requires further investigation.

Finally, it is well known that the decomposition of BP can also be brought about by the action of u. v. light. Experiments carried out with labeled compounds showed that during photolysis of BP in benzene solution, biphenyl is obtained at the expense of phenyl radicals from the peroxide (Experiments 9 and 10). The presence of a small amount of phenyl groups from benzene can probably be explained by the concurrent occurrence of the slower thermal reaction. Thus, the following reaction takes place under the influence of light:

$$BP \xrightarrow{h\nu} BP^{*} \rightarrow C_6H_5 - C_6H_5 + 2CO_2.$$

We also used a similar method to investigate the reaction of lead tetrabenzoate (LTB) with benzene. As is well known, tetravalent lead derivatives readily decompose and are converted into derivatives of divalent lead. During such a decomposition of LTB, two benzoate radicals must be liberated; these are the same radicals as are formed during the decomposition of BP. When LTB is heated in benzene, lead dibenzoate and CO_2 separate, and biphenyl and benzoic acid are formed. Using labeled compounds (Experiments 11), it was possible to establish that, within the limits of experimental error, the biphenyl was obtained from LTB and benzene according to the over-all equation:

$$Pb(OCOC_6H_5)_4 + C_6^{*}H_6 \rightarrow Pb(OCOC_6H_5)_2 + C_6^{*}H_5 - C_6H_5 + C_6H_5COOH + CO_2.$$

When labeled LTB was used (Experiment 12), the transition of phenyl radicals to benzene was not noted.

The final subject of investigation in the present work was nitrosoacetanilide (NAA). It is well known that it

readily isomerizes into the diazoacetate, and the latter decomposes with the liberation of nitrogen and the formation of a phenyl radical. The reaction of NAA with benzene proceeds according to the equations:

$$C_6H_5N(NO)COCH_3 \rightarrow C_6H_5N = NOCOCH_3 \xrightarrow{C_6H_6} C_6H_5 - C_6H_5 + N_2 + CH_3COOH.$$

By using labeled NAA in ordinary benzene (Experiment 14) and in labeled benzene (Experiment 13) it was possible to show that in this case biphenyl is obtained from phenyl radicals from NAA and benzene. The conversion of phenyl radical to benzene was not detected. There no cause to doubt that the latter reaction proceeds homolytically, but it has a closed radical mechanism. It seems to us that methods in which radicals are transferred from the reaction cage into the solution can be widely used in investigations of the mechanism of free radical reactions in the liquid phase.

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THE ADDITION OF SILANES TO UNSATURATED COMPOUNDS IN THE PRESENCE OF IRON PENTACARBONYL

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As has previously been reported by us together with A. N. Nesmeyanov, olefins undergo thermal telomerization reactions with various silanes according to the scheme [1]:

$$HSiX_3 + n\,CH_2 = CHR \xrightarrow{300^\circ} SiX_3(CH_2CHR)_nH.$$

The use of this reaction is limited owing to decomposition of olefins containing functional substituents and polymerization of α-olefins under the vigorous telomerization conditions; therefore, it was necessary to find a catalyst which would permit the use of a lower reaction temperature.

When the process is carried out in steel autoclaves, peroxides and azo compounds do not initiate telomerization of olefins with silicon compounds containing an Si-H bond [2]; this is evidently due to an inhibiting effect of the autoclave walls [3].

We investigated the compounds shown in Table 1 as possible initiators (catalysts).

Of the compounds enumerated, only $H_2PtCl_6 \cdot 6H_2O$ and $4C_2H_5 \cdot NiCl_2$ have been investigated as catalysts for the addition of silanes to olefins [3,4].

As may be seen from Table 1, a wide range of compounds catalyze the reactions between olefins and silanes. However, only in the presence of $TiCl_4$ and $H_2SnCl_6 \cdot 6H_2O$ does the reaction lead to the formation of a mixture of homologous telomers; in the remaining cases, only the addition of the silanes to the olefins occurred (see Table 2).

Iron pentacarbonyl was the most interesting of the catalysts found in this work. It catalyzed the reaction between olefins and silanes at 100-140°. Silicon tetrachloride and methoxytrichlorosilane did not add to ethylene in the presence of $Fe(CO)_5$.

We studied the reaction of ethylene with methyldichlorosilane, triethoxysilane, and triethylsilane of propylene with methyldichlorosilane, and of vinyl ethyl ether with triethylsilane in the presence of $Fe(CO)_5$. These reactions gave yields of 60-85 % of theoretical.

As is well known, the reaction of triethyl- and triethoxysilanes with ethylene does not go either in the presence of radical initiators or on heating to 250-300°, or else the reaction gives only a small yield of the addition product [5].

The reaction between triethylsilane and vinyl ethyl ether in the presence of $Fe(CO)_5$ was very interesting. In this case, the major product was apparently β-ethoxyvinyltriethylsilane, the structure of which was verified by investigation of the infrared spectrum. Acid hydrolysis of this compound, which was carried out under relatively vigorous conditions, led to the formation of hexaethyldisiloxane.

Kharasch and co-workers observed the similar formation of an unsaturated product having the structure $C_6H_5CH = CHSO_3Na$, in the case of the homolytic addition of $NaHSO_3$ to styrene [6].

TABLE 1

Group of periodic system	Compounds
IV	$TiCl_4$, K_2TiCl_6[1], Rb_2TiCl_6, TiO_2, $ZrCl_4$, Et_2ZrCl_2, $(C_5H_7O_2)_4Zr$, ZrO_2, $(C_{10}H_7O_2)_2ZrCl_2$[1], $(C_{10}H_7O_2)_4Zr$, $Zr(NO_3)_4$, $Et_2Si(C_2H_3)_2$, $SnCl_4$, $Sn(C_2H_3)_4$, $H_2SnCl_6 \cdot 6H_2O$
V	$VOCl_3$, $NbOCl_3$[2], Et_2NbCl_3.
VI	$CrCl_3$, $Cr(CO)_6$, $CrCl_2$[2], $Mo(CO)_6$, $MoCl_5$[2], $W(CO)_6$ WCl_6[2]
VIII	$Fe(CO)_5$, $(C_{10}H_7O_2)_3FeCl$; $CoCl_2$, $(C_5H_7O_2)_2Co$; $NiCl_2 \cdot 4C_5H_5N$, $H_2PtCl_6 \cdot 6H_2O$

1 The compounds which are struck out were inactive.

2 These compounds were tested in the reaction of methyldichlorosilane with 1-hexene, and they gave positive results.

TABLE 2

$CH_3SiCl_2H + nRCH = CH_2 \rightarrow CH_3SiCl_2(RCHCH_2)_nH$

Catalyst	Amount of catalyst	CH_3SiCl_2H used, g	Change in pressure, atm.	Temp., deg C	Wt. of products discharged, g	Yield, % of silane reacted	Reaction time, hr	n[4]
Experiments with ethylene								
$H_2PtCl_6 \cdot 6H_2O$	0.1 ml[3]	58	30—1	20—30	66	93	0.5	1
$Fe(CO)_5$	1 ml	173	80—45	130—140	201	62	0.5	1
$Fe(CO)_5$	1 ml	72	520—490	130—140	77	70	1.5	1
$ZrCl_4$	0.2 g	135	80—40	170—180	149	81	1	1
$ZrCl_4$	0.2 g	132	170—120	170—180	156	76	1	1
$TiCl_4$	0.5 g	135	210—120	190—200	153	60	6	1.2
$H_2SnCl_6 \cdot 6H_2O$	2 ml	128	360—220	210—220	185	90	3.5	1—3
Experiments with propylene								
$H_2PtCl_6 \cdot 6H_2O$	0.1 ml[3]	65	10—1	20—30	86	92	1	1
$H_2SnCl_6 \cdot 6H_2O$	2 ml	136	190—70	210—220	221	80	4	1—2
$Fe(CO)_5$	1 ml	58	60—40	125—135	71	70	2	1
$TiCl_4$	0.5 g	124	240—120	165—170	167	80	6	1—2

1 The reaction was carried out with excess olefin.

2 The reaction products were distilled in a column of 15 theoretical plates. The constants of the compounds obtained were in agreement with the constants of the thermal telomerization products previously described by us [1]. In the Table, n = 1 indicates that higher telomers were not formed.

3 A solution of 0.00325 g of $H_2PtCl_6 \cdot 6H_2O$ in 0.1 ml of isopropyl alcohol.

4 These values are conversions of the original methyldichlorosilane.

In our case, there is apparently an analogous reaction, and the formation of β-ethoxyvinyltriethylsilane is associated with the ease of dehydrogenation of the intermediate radical $(C_2H_5)_3SiCH_2 \cdot \dot{C}HOC_2H_5$.

That the reaction taking place in the presence of iron pentacarbonyl is a radical reaction is indicated by the formation of symmetrical hexaethyldisilylethane and hexaethoxydisilylethane as by-products in the reaction of ethylene with triethylsilane and triethoxysilane.

The formation in these reactionsof symmetrical hexaalkyldisilylethanes is difficult to understand except as the products of the homolytic recombination of $X_3SiCH_2CH_2^{\cdot}$ and $SiX_3^{\cdot}$ radicals.

Another possibility for the formation of symmetrical hexaethyldisilylethane is the reaction of ethylene with hexaethyldisilane [7, 8] (which could be formed by the recombination of two $Si(C_2H_5)_3$ radicals) according to one of the following schemes:

$$1)\ Si(C_2H_5)_3^{\cdot} + Si(C_2H_5)_3^{\cdot} \rightleftarrows Si(C_2H_5)_3 - Si(C_2H_5)_3$$

$$2Si(C_2H_5)_3^{\cdot} + CH_2 = CH_2 \rightarrow (C_2H_5)_3SiCH_2CH_2Si(C_2H_5)_3$$

or

$$2)\ Si_2(C_2H_5)_6 \xrightarrow{\text{rearrangement [8]}} (C_2H_5)_3SiC_2H_4Si(C_2H_5)_2H \xrightarrow{C_2H_4}$$

$$\rightarrow (C_2H_5)_3SiCH_2CH_2Si(C_2H_5)_3.$$

However, we are able to show that under the reaction conditions described, hexaethyldisilane does not react with ethylene, and, consequently, the reaction does not proceed by either one of the two schemes presented above.

It should be noted that Harmon [9] observed the formation of a symmetrical product during the homolytic telomerization of ethylene with hydrogen sulfide; among other substances, a compound having the structure $C_2H_5SCH_2CH_2SC_2H_5$ was isolated.

EXPERIMENTAL PART

The experiments were carried out in 0.5-liter steel autoclaves. A "blank" experiment was carried out each time a change to a new catalyst was made. It should be pointed out that in all cases except iron pentacarbonyl, which apparently decomposed completely during the course of a single experiment, it was necessary to turn down the walls of the autoclave with a lathe, since the autoclave walls retained catalytic activity without the addition of new portions of catalyst.

Reaction of triethylsilane and triethoxysilane with ethylene in the presence of $Fe(CO)_5$. The reaction was carried out in a halfliter autoclave. 34.4 g of $(C_2H_5)_3SiH$ and 1 ml of $Fe(CO)_5$ were charged to the autoclave, the autoclave was purged with nitrogen, and ethylene was then introduced to a pressure of 45 atm. The reaction mixture was heated to 100°. The reaction was carried out at this temperature for two hours.

39.5 g of reaction products was obtained. Distillation gave 34.5 g (81% of theoretical) of $(C_2H_5)_4Si$, b.p. 151°, d_4^{20} 0.7635, n_D^{20} 1.4250 MR found; 48.34; calculated for $C_8H_{20}Si$, 48.78.

See reference [1] for literature values.

After distillation of the $(C_2H_5)_4Si$, a fraction boiling at 117°, 8 mm, n_D^{20} 1.4592, d_4^{20} 0.8232, was collected. MR found, 85.72; calculated for $(C_2H_5)_3SiCH_2]_2$, 86.22. Literature data [10]: b.p. 265-267°, n_D^{20} 1.4582, d_4^{20} 0.8222.

Found %: C 65.21; 65.37; H 12.56; 12.71; Si 21.85; 21.77; $C_{14}H_{34}Si_2$. Calculated %: C 65.53; H 12.57; Si 21.89.

The reaction of triethoxysilane with ethylene was carried out by the procedure described above. 41 g of $(C_2H_5O)_3SiH$ and an excess of ethylene were heated in the presence of 0.5 ml of $Fe(CO)_5$ at 130° for 3 hours; 48 g of reaction products was obtained. Distillation in a column gave 31 g (65% of theoretical) of $(C_2H_5O)_3SiC_2H_5$, b.p. 80-81° at 40 mm, n_D^{20} 1.3935; d_4^{20} 0.9037 MR found 50.84; MR calc. 51.24.

Found %: Si 14.41; 14.33; $C_8H_{20}O_3Si$. Calculated %: Si 14.60.

After distillation of the $(C_2H_5O)_3SiC_2H_5$, a fraction boiling at 102-103° at 5 mm was collected; n_D^{20} 1.4052, d_4^{20} 0.9587. MR found 90.67; calculated for $[(C_2H_5O)_3SiCH_2]_2$, 91.14. Literature data [10]: n_D^{20} 1.4120; d_4^{20} 0.9660.

Reaction of triethylsilane with vinyl ethyl ether. A mixture of 42 g of $(C_2H_5)_3SiH$ and 39 g of $C_2H_5OCH = CH_2$ was heated in the presence of 1 ml of $Fe(CO)_5$ at 130° for one hour. Distillation of the reaction products gave 22 g of $C_2H_5OCH = CH_2$ (b.p. 35°), 19 g of $(C_2H_5)_3SiH$ (b.p. 106-108°), and 9.8 g of another product (b.p. 78-80° at 10 mm). MR found, 59.31; calculated for $(C_2H_5)_3SiCH = CHOC_2H_5$, MR 59.38.

Found %: C 64.23; 64.07; H 11.79; 11.82; Si 15.06; 14.09. $C_{14}H_{32}SiO$. Calculated %: C 64.45; H 11.90 Si 15.06.

The infrared spectrum had an intense band at 1615 cm^{-1}, which is characteristic of a double bond.

The hydrolysis of $(C_2H_5)_2SiCH = CHOC_2H_5$ was carried out by heating 5 g of the substance with 3 g of 2% H_2SO_4 at 110° for 6 hours; the reaction mixture was vigorously stirred. Distillation of the reaction products gave a fraction boiling at 68-71° at 3 mm, n_D^{20} 1.4370; d_4^{20} 0.8437. MR found 76.65; calculated for $(C_2H_5)_2SiOSi(C_2H_5)_2$ MR 76.35.

Found %: C 58.65, 58.59; H 12.18, 12.13; Si 22.73, 22.90; $C_{12}H_{30}Si_2O$. Calculated %: C 58.46; H 12.26; Si 22.79.

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THE BEHAVIOR OF ZINC OXIDE IN OXIDE MELTS

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The literature contains little information on the effect of zinc oxide on the properties of slags. Attempts to measure the viscosity of oxide melts containing zinc oxide have been unsuccessful. Ferrous melts containing zinc oxide froth and do not form a homogeneous liquid. The present work undertook the problem of establishing the reason for the frothing of zinc-containing oxide melts and of explaining the evolution of zinc vapors from the slag when it is removed from a lead shaft furnace.

The experimental method consisted basically of melting a mixture of iron, silicon, calcium, and zinc oxides in a protected quartz tube in an induction furnace. A tungsten crucible was used as the heater. The oxides were carefully ground in a mortar and mixed, and the mixture was then placed in a corundum crucible and given a preliminary calcination in a muffle furnace at 1000°. A corundum crucible containing a weighed portion of a mixture of the pure oxides or silicates was placed inside the tungsten crucible, which was then placed inside the quartz tube. The temperature was measured with a platinum–platinum-rhodium thermocouple, the end of which was submerged in the melt. The temperature of the melt reached the desired value within 10-12 minutes, after which the melt was held at this temperature for 30 minutes and then cooled. In Table 1 are presented the experimental data for individual metal oxides and for mixtures containing zinc oxide, ferric oxide, and silica. On heating for 30 minutes at 1600°, zinc oxide which had first been calcined at 900° lost a total of 1.15% by volatilization. Heating and fusing Fe_2O_3 at temperatures above 1600° led to dissociation with the formation of magnetite and ferrous oxide. Thus, 24% ferrous oxide was found in an Fe_2O_3 melt which had been soaked for 30 minutes.

When a mixture of ferric oxide and zinc oxide was heated at temperatures of up to 1600°, frothing of the slag occurred, and, if the experiment was carried out in air, a white oxide deposit appeared on the cold parts of the quartz tube. In an atmosphere of argon, the deposit on the cold parts of the tube had a silvery, metallic color. The metallic deposit and the oxide which deposited on the cold parts of the tube were well washed with acidified Low solution. Analysis of the solution showed that it contained zinc. Evolution of hydrogen was observed when the silvery metallic deposit was washed with hydrochloric acid. As may be seen in Table 1, 51-78.6 % of the ZnO in the binary mixtures was reduced, the amount depending on the ratio of iron to zinc.

The introduction of silica into the melt lowered the reducibility of the zinc oxide by tying the zinc up as the silicate. When a melt corresponding to the stoichiometric composition of willemite ($2ZnO \cdot SiO_2$) was heated at high temperatures, the zinc was not volatilized.

Fusion of a mixture of zinc silicate and ferrous silicate and subsequent soaking of the melt at a temperature of 1400° led to reduction and volatilization of up to 25% of the ZnO.

The introduction into zinc silicate melts of even an insignificant amount of ferrous silicate led to reduction of the zinc oxide. Heating mixtures of willemite ($2ZnO \cdot SiO_2$) and Fe_2O_3 at temperatures of 1400° led to reduction and volatilization of the zinc oxide.

In Table 2 are presented the results of determinations of the reduction of zinc oxide in melts containing zinc oxide together with silica and calcium oxide. The presence of calcium oxide in the melts did not produce a homogeneous liquid state; the melt frothed, and the zinc oxide was reduced. From 15 to 25% of the zinc oxide was reduced in thirty minutes at a temperature of 1400°, the amount of reduction depending on the composition

TABLE 1

Behavior of Zinc Oxide in Ternary Silicate Melts

Starting Material	Calcd. chemical compn. of the oxide mixts., %			Temperature deg C	Time, min	% Redn. of ZnO	Chemical compn. of melt, %		
	Fe_2O_3	SiO_2	Zn				FeO	Fe_2O_3	Zn
Fe_2O_3	100,0	—	—	1600°	30,0	—	24,0	76,0	—
ZnO	—	—	100,0	1600°	30,0	1,15	—	—	—
Fe_2O_3 + ZnO	95,0	—	5,0	1600°	30,0	78,6	49,25	48,32	2,10
	85,0	—	15,0	1600°	30,0	51,0	—	—	—
$2ZnO \cdot SiO_2$	—	30,0	70,0	1550°	30,0	0,00	—	—	—
$2ZnO \cdot SiO_2$ +	6,0	24,0	70,0	1400°	30,0	9,00	4,0	3,98	58,68
+ $2FeO \cdot SiO_2$	36,0	27,0	37,0	1400°	30,0	25,2	5,38	26,72	48,36
Mixture of powdered	5,0	50,0	45,0	1540°	30,0	11,1	1,68	3,82	—
oxides	25,0	50,0	25,0	1500°	30,0	27,5	9,08	11,46	15,10
Fe_2O_3:SiO_2:ZnO	45,0	50,0	5,0	1500°	30,0	20,0	—	—	—
$2ZnO \cdot SiO_2$ +	8,0	43,5	48,5	1400°	30,0	18,0	21,89	25,22	25,79
+ α Fe_2O_3	31,0	32,0	37,0	1400°	30,0	10,0	—	—	—
	58,0	21,0	21,0	1400°	30,0	1,5	—	—	—

TABLE 2

Calculated chemical composition of oxide mixtures				Temperature, deg C	Time, min.	% Redn. of ZnO	Chemical composition of melts		
FeO	SiO_2	CaO	ZnO				FeO	Fe_2O_3	ZnO
5,0	40,0	20,0	35,0	1400	30,0	15,10	2,75	3,87	18,13
5,0	40,0	20,0	35,0	1300	30,0	3,50	3,05	3,11	25,48
5,0	40,0	20,0	35,0	1200	30,0	2,40	3,61	2,60	23,95
10,0	40,0	40,0	10,0	1400	30,0	23,20	4,54	7,16	1,92
10,0	40,0	40,0	10,0	1300	30,0	8,80	7,82	0,98	4,85
10,0	40,0	40,0	10,0	1200	30,0	8,00	5,64	3,50	5,37
10,0	27,0	33,0	30,0	1400	30,0	25,0	—	—	—
10,0	27,0	33,0	30,0	1300	30,0	9,30	4,87	5,49	21,48
10,0	27,0	33,0	30,0	1200	30,0	7,80	5,92	5,01	23,5
20,0	27,0	33,0	20,0	1300	30,0	8,36	1,62	18,68	17,78
30,0	27,0	33,0	10,0	1300	30,0	9,55	2,65	26,88	2,10

of the slag. Lowering the soaking temperature to 1200° led to a decrease in the amount of zinc sublimed. More complete reduction occurred in melts having a lower viscosity and in which less of the zinc oxide was combined as the corresponding silicates.

Discussion of Results. As a result of this work, it was established that melts containing ferric oxide and zinc oxide are not homogeneous liquids. At temperatures at which the liquid state exists, reduction and evaporation of metallic zinc occurs. Since the oxides SiO_2 and CaO remain unchanged when heated, only the lower oxides of iron can act as reducing agents. The melts were not ferromagnetic after cooling to room temperature, which indicates that neither metallic iron nor magnetite are present in the melts. At the same time, analysis showed that the melts contained ferric oxide. The presence of nonmagnetic α-Fe_2O_3 in the cooled melt indicated its secondary origin. In connection with this, it can be assumed that the following oxidation-reduction reaction takes place in liquid melts containing ferric oxide and zinc oxides

$$ZnO + FeO \rightarrow Zn\uparrow + Fe_2O_3\downarrow$$

the resulting zinc is lost by volatilization.

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HYDROGENOLYSIS OF CARBONYL-CONTAINING FURAN COMPOUNDS. CONVERSION OF ALKYLACYLFURANS TO SIX-MEMBERED CARBOCYCLIC COMPOUNDS

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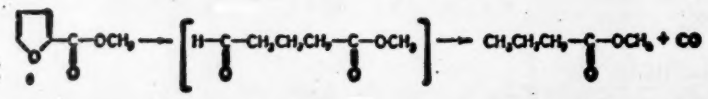
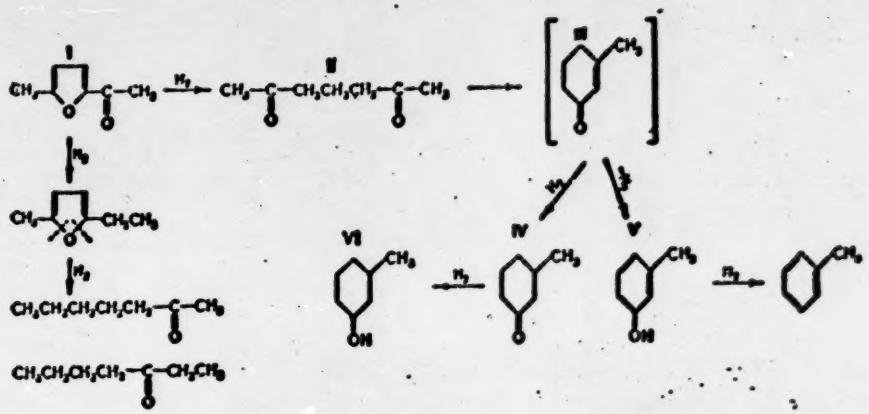
As numerous investigations have shown, the direction of hydrogenolysis of the furan ring depends on various factors, and first of all on the nature of the catalyst and the properties of any side chain present. Thus, when sylvan and furfuryl alcohol are hydrogenated in the liquid phase in the presence of Adams platinum catalyst, cleavage of the furan ring occurs at the C—O bond not adjacent to the side chain, while hydrogenolysis of pyromucic acid under these same conditions proceeds at the C—O bond next to the carboxyl group [1]. Definite conclusions relative to the effect of side chains on the site at which the furan ring opens during hydrogenolysis is possible only through a comparison of experimental data obtained during hydrogenation of furan compounds under uniform conditions of phase and pressure. The necessity for uniform conditions is shown by the experimental fact that when sylvan is hydrogenated in the vapor phase at ordinary pressure over copper chromite, hydrogenolysis proceeds in only one direction, specifically, at the 1,5-C—O bond with the formation of methyl propyl ketone [2], while in the liquid phase under elevated hydrogen pressure, hydrogenolysis proceeds in both possible directions, at the 1,2- and 1,5-C—O bonds with the formation of, respectively, 1-pentanol and 2-pentanol [3]. Vapor-phase hydrogenation conditions sometimes completely change the nature and succession of the reactions taking place. Hydroxyl and carbonyl groups located in the vicinity of the furan ring are reduced under vapor-phase conditions over nickel catalyst (Ni/ZnO and Ni/CdO) before hydrogenation or hydrogenolysis of the furan ring [4], while in the liquid phase, reduction of the hydroxyl or carbonyl group with retention of the furan ring does not take place to any extent. We previously investigated the effect of the alkyl group in α-alkylfurans on the course of the hydrogenolysis of the furan ring under vapor-phase hydrogenation conditions over Pt/C catalyst under ordinary pressure, and we found that under these conditions, cleavage of the furan ring occurs exclusively at the C—O bond not next to the alkyl radical, which resulted in the formation of aliphatic ketones.

In the present work, we investigated the hydrogenation of the methyl ester of pyromucic acid and 2-methyl-5-acetylfuran under conditions which were completely analogous to those used in the hydrogenation of α-alkylfurans. We found that in this case the carbonyl-containing groups exerted a decisive effect on the direction of cleavage of the furan ring, but the effect of these groups was contrary to the alkyl-radical effect. In both cases, hydrogenolysis of the furan ring proceeded readily and exclusively at the C—O bond adjacent to the carbonyl-containing groups. During the process, the initially formed hydrogenolysis products undergo further conversion under the vapor-phase hydrogenation conditions; this is, on the one hand, undoubtedly of theoretical interest, and, on the other hand, it opens up new possibilities for the synthesis of valuable compounds on the basis of furfural. Thus, we found that methyl butyrate is formed in about 95% yield during the hydrogenation of the methyl ester of pyromucic acid at 275° over Pt/C; the methyl butryate results from the decarbonylation of the intermediately formed ester of the corresponding aldehydic acids



A very interesting conversion occurs during hydrogenation of 2-methyl-5-acetylfuran over this same catalyst; among the major products are 3-methylcyclohexanone, 3-methylcyclohexanol, and meta cresol. The formation of carbocyclic compounds during the hydrogenation of 2-methyl-5-acetylfuran presumes deep structural changes in the molecule of this heterocyclic ketone, and it is definitely the result of a series of successive reactions. The course of this process could be the following: hydrogenolysis of the furan ring at the 1,5-C—O bond to give 2 6-heptanedione (II), which then undergoes cyclization to 1-methyl-1-cyclohexene-3-one (III) by a reaction analogous to that which occurs during the treatment of δ-diketones with acids and bases [6]. The 1-methyl-1-cyclohexene-3-one can then undergo conversion to 3-methylcyclohexanone (IV) or meta cresol (V).



It is clear that the conversion of III to V will take place more completely at an elevated temperature, and, on the contrary, a low temperature will favor the occurrence of the reactions III → IV — VI. In fact, the catalyzate from the hydrogenation of 2-methyl-5-acetylfuran at 270-300° contains about 50% meta cresol, and 3-methylcyclohexanone is absent, while at 215-220°, ~25% 3-methylcyclohexanone is formed (in a mixture also containing 3-methylcyclohexanol), and there is practically no meta cresol present. When 2-methyl-5-acetylfuran is passed over the catalyst at a low rate, a small part of the meta cresol may be converted to toluene.

Thus, in contrast to nickel catalysts, with which the primary reaction during hydrogenation of 2-methyl-5-acetylfuran is reduction of the carbonyl group, the chief reaction over Pt/C catalyst is hydrogenolysis of the ring at the C—O bond next to the carbonyl group, and this is followed by successive reactions leading to the formation of carbocyclic compounds (3-methylcyclohexanone and meta cresol). Initial reduction of the carbonyl group of 2-methyl-5-acetylfuran over Pt/C also occurs, but to a degree which is considerably less than over nickel catalysts.

The direct conversion of I to IV and V obviously has general significance and can serve as a new method for the catalytic synthesis of alkylcyclohexanones from 2-alkyl-5-acylfurans.

The hydrogenation of 2-methyl-5-acetylfuran and the methyl ester of pyromucic acid was carried out in a flow-type apparatus at ordinary pressure and at different temperatures: 215-220°, 275°, and 300°. The furan compound was fed to the catalyst at a space rate of 0.1 hours^{-1}. The catalyst was platinized carbon containing 10% platinum, and was prepared by impregnation of activated with a chloroplatinic acid solution followed by reduction with hydrogen in the reaction tube at 250-320°. The reaction products were distilled in an efficient fractionating column.

1. Methyl butyrate: b.p. 102-102.5°, d^{20} 0.8979, n_D^{20} 1.3870.

2. Meta cresol: b.p. 201-203°, 45-45.5° (1 mm), d_4^{20} 1.0320; n_D^{20} 1.5380.

3. 3-Methylcyclohexanone: b.p. 168.2-168.5° (744 mm), d_4^{20} 0.9129; n_D^{20} 1.4453. After recrystallization from methyl alcohol, the semicarbazone melted at 179-180°.

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COMPLEX FORMATION AND PHASE TRANSFORMATIONS IN THE RECIPROCAL QUATERNARY SYSTEM OF THE CHLORIDES AND SULFATES OF LITHIUM, SODIUM AND POTASSIUM

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Development of the chemistry of fused salts and the accumulation of a large amount of material relating to equilibrium diagrams show that in melts, complex formation between salts is considerably greater and more variegated than in aqueous solutions of these same salts.

The considerably fewer complex compounds formed in aqueous solutions is due to the significant occurrence of hydration of the salts, this predominating, in many cases, over the process of complex formation. The results of our investigations of the melting diagrams of the reciprocal quaternary system Li, Na, K‖Cl, SO_4 (Figure 1) constitute an illustration of the above.

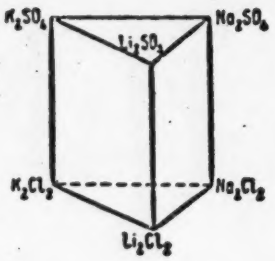

Fig. 1

As is well known, in aqueous solutions only one compound, $Na_2SO_4 \cdot 3K_2SO_4$ (glaserite), is formed between Na and K sulfates; this compound is widely encountered in potassium sulfate deposits. In the absence of water, there is a single compound formed during decomposition of solid solutions of the above elements below 476°. But these solid solutions in the ternary system Ni, Na, K ‖ SO_4 decompose with the formation of three compounds when the temperature is raised to 784-816°; the composition of these compounds have not been accurately established, nor has any one of them been identified with the compound stable below 476°. The decomposition temperatures of these solid solutions decrease in the presence of the chlorides of these same elements. For example, this occurs in the range of 686-736° in the system Na, K ‖ Cl, SO_4. The accumulated material on fused and aqueous multicomponent salt systems indicates the great significance of thermodynamic conditions in complex formation, particularly in the presence of other components in the liquid phase.

Moreover, a directional effect of solvents on the composition and structure of some complex compounds has been established. All of this indicates a significant effect of the medium and of the solvent on complex formation. The study of this phenomenon constitutes one of the most important problems in the investigation of the chemistry of multicomponent systems.

In an investigation of the fusion products of the reciprocal quaternary system mentioned above, Li, Na, K ‖ $ClSO_4$ (Figure 1) [1-9], 17 complex compounds were established, and of these, five were double salts on the edges of the triangular composition prism (Figure 2), and three ([I], [II], [III]) were formed during decomposition of solid solutions of Na and K sulfates.

The investigation of the fusion products of the reciprocal quaternary system mentioned above, Li, Na, K ‖ $ClSO_4$

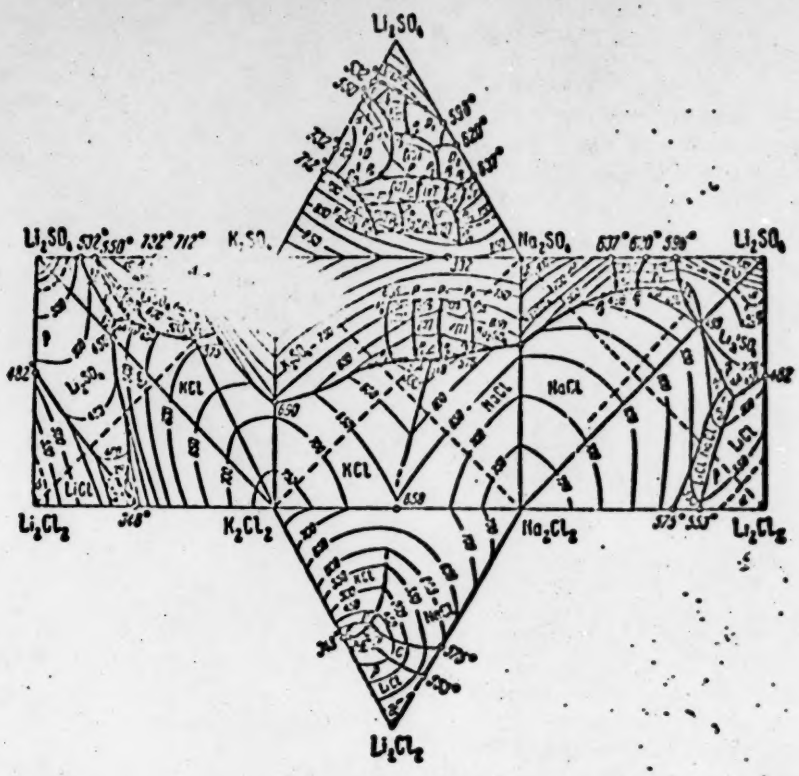
Li_2SO_4
K_2SO_4
Na_2SO_4
Li_2SO_4
Li_2SO_4
KCl
NaCl
LiCl
Li_2Cl_2
K_2Cl_2
Na_2Cl_2
Li_2Cl_2

Fig. 2

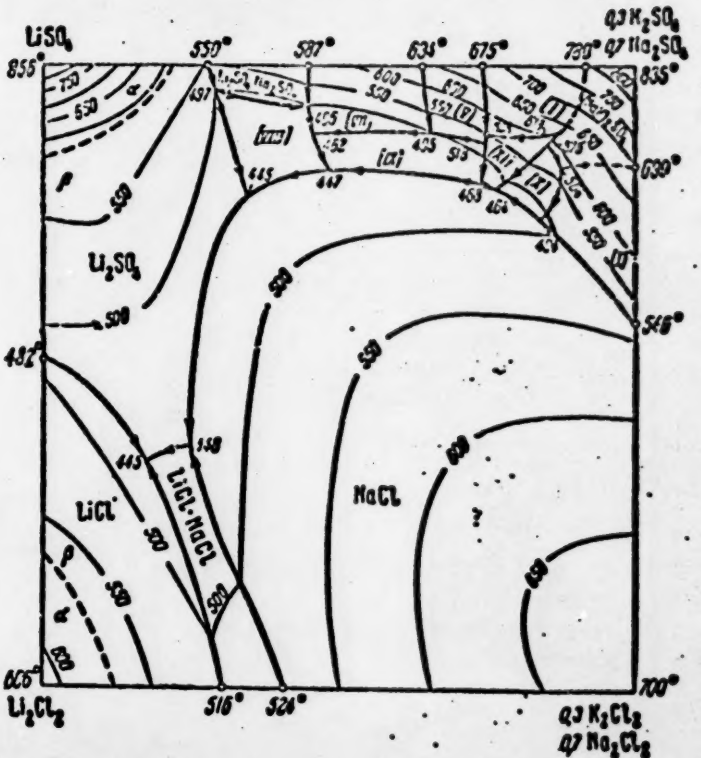
$LiSO_4$
550°
587°
634°
675°
735°
q3 K_2SO_4
q7 Na_2SO_4
855°
835°
839°
Li_2SO_4
482°
546°
LiCl
LiCl-NaCl
NaCl
605°
516°
526°
700°
Li_2Cl_2
q3 K_2Cl_2
q7 Na_2Cl_2

Fig. 3.

TABLE 1*

Phase tetrahedron No.	Quadruple point	Temperature, deg C	Composition in ion% on the lateral face of the prism				Equilibrium phases
			Li, Na ‖ Cl, SO_4				
			Li^+	Na^+	Cl^-	SO_4^{--}	
I	E_1	316	92,0	8,0	93	7	LiCl·NaCl, LiCl, KCl, Li_2SO_4
II	E_2	410	64,4	35,6	26,3	73,7	D, [IX], NaCl, KCl
III	E_3	430	91,0	9,0	23,7	76,3	G, [VIII], NaCl, Li_2SO_4
IV	E_4	444	69,6	30,4	10,8	89,2	D_1, [VIII], [IX], NaCl
V	E_5	445	60,4	39,6	12,0	88,0	[VII], [VIII], [IX], NaCl
VI	E_6	446	73,0	27,0	22,5	77,5	[VIII], [IX], KCl, K_2SO_4
VII	E_7	448	52,0	48,0	11,3	88,7	D_1, D_2, [IX], NaCl
VIII	E_8	454	51,4	48,6	9,0	91,0	D_1, D_2, [VII], [IX]
IX	E_9	458	21,0	79,0	24,7	75,4	[I], [XI], NaCl, KCl
X	E_{10}	464	35,0	65,0	12,5	77,5	[V], [IX], NaCl, Na_2SO_4
XI	E_{11}	466	36,6	63,4	11,5	88,5	D_2, [IX], [X], $NaSO_4$
XII	E_{12}	468	35,5	64,5	11,7	88,3	D_2, [X], NaCl, Na_2SO_4
XIII	E_{13}	486	22,3	77,3	26,2	73,8	[II], [III], [XII], KCl
XIV	E_{14}	490	43,0	57,0	11,6	88,4	[V], [VI], [VII], [IX]
XV	E_{15}	520	30,3	69,7	11,8	88,2	[I], [IV], [V], [X]
XVI	E_{16}	545	31,0	69,0	11,5	88,5	[I], [III], [V], [XI]
XVII	E_{17}	548	37,2	62,8	11,5	88,5	[II], [III], [VI], [XII]
XVIII	E_{18}	550	37,7	62,3	11,8	88,2	[III], [VI], [IX], [XII]
XIX	P_1	364	83,0	17,0	17,0	83,0	LiCl·NaCl, KCl, NaCl, Li_2SO_4.
XX	P_2	440	95,0	5,0	24,2	75,8	D, G, NaCl, KCl
XXI	P_3	444	91,0	9,0	22,0	78,0	D, G, [VIII], NaCl
XXII	P_4	445	97,0	3,0	24,0	76,0	G, NaCl, KCl, Li_2SO_4
XXIII	P_5	446	33,0	67,0	22,0	78,0	[IX], [XI], NaCl, KCl
XXIV	P_6	450	61,6	38,4	11,5	88,5	D_1, [VII], [VIII], NaCl
XXV	P_7	454	68,0	32,0	11,4	88,6	D_1, [IX], NaCl, Li_2SO_4
XXVI	P_8	460	18,0	82,0	25,5	74,5	[I], [X], [XI], KCl
XXVII	P_9	463	32,0	68,0	22,5	77,5	[IX], [XI], [XII] KCl
XXVIII	P_{10}	465	19,4	80,6	25,2	74,8	[I], [II], [X], KCl
XXIX	P_{11}	467	29,6	70,4	20,8	79,2	[IX], [X], [XI], NaCl
XXX	P_{12}	476	72,0	28,0	11,2	88,8	D, [VII], [VIII], [IX]
XXXI	P_{13}	478	34,5	65,5	11,5	88,5	D_2, [IV], [IX], Na_2SO_4
XXXII	P_{14}	491	38,0	62,0	27,5	72,5	[IX], [XII], KCl, K_2SO_4
XXXIII	P_{15}	492	18,0	82,0	27,0	73,0	[I], [II], NaCl, KCl
XXXIV	P_{16}	500	33,7	66,3	14,5	85,5	[VI], [IX], [X], [XI]
XXXV	P_{17}	508	40,6	59,4	9,5	90,5	D_2, [V], [VII], [IX]
XXXVI	P_{18}	510	16,0	84,4	24,0	76,0	[I], [X], NaCl, Na_2SO_4
XXXVII	P_{19}	515	24,0	76,0	28,0	72,0	[III], [XII], KCl, K_2SO_4
XXXVIII	P_{20}	518	46,6	53,4	26,0	74,0	D, [IX], KCl, K_2SO_4
XXXIX	P_{21}	520	34,6	65,4	7,4	92,6	D_2, [IV], [V], [IX]
XXXX	P_{22}	540	36,5	63,5	13,5	86,5	[II], [IX], [XI], [XII]
XXXXI	P_{23}	542	25,5	74,5	11,4	88,6	[I], [IV], [X], Na_2SO_4
XXXXII	P_{24}	554	59,5	40,5	12,5	87,5	D, [VI], [VII], [IX]
XXXXIII	P_{25}	552	32,0	68,0	11,6	88,4	[II], [V], [VI], [IX]
XXXXIV	P_{26}	560	29,0	71,0	12,5	87,4	[I], [V], [XI], [XII]
XXXXV	P_{27}	570	53,5	46,5	11,7	88,3	D, [VI], [IX], K_2SO_4
XXXXVI	P_{28}	580	47,3	52,7	11,5	88,5	[III], [VI], [IX], K_2SO_4

* G = $2Li_2SO_4$; D = $LiSO_4 \cdot K_2SO_4$; D_1 = Li_2SO_4; D_2 = $Li_2SO_4 \cdot 2Na_2SO_4$. Internal phases: [I], [II], [III], [IV], [V], [VI], [VII], [VIII], [IX], [X], [XI], [XII]; E) quadruple eutectic point; P) quadruple transition point.

(Figure 1) demonstrated their extreme tendency toward interaction, a tendency approaching that of the borates and silicates.

The external faces of the prism are shown opened out in Figure 2. It may be seen that Li and Na sulfates form two compounds: $Li_2SO_4 \cdot Na_2SO_4$ and $Li_2SO_4 \cdot 2Na_2SO_4$, and their chlorides form one, LiCl·NaCl; two compounds are also formed between Li and K sulfates: $Li_2SO_4 \cdot K_2SO_4$ and $2Li_2SO_4 \cdot K_2SO_4$. The solid solutions inside the system decompose into three independent phases ([I], [II], and [III]). There are 5 internal phases — [IV], [V], [VI], [VII], and [VIII] — appearing as ternary sulfates, in the system Li, Na, K ‖ SO_4.

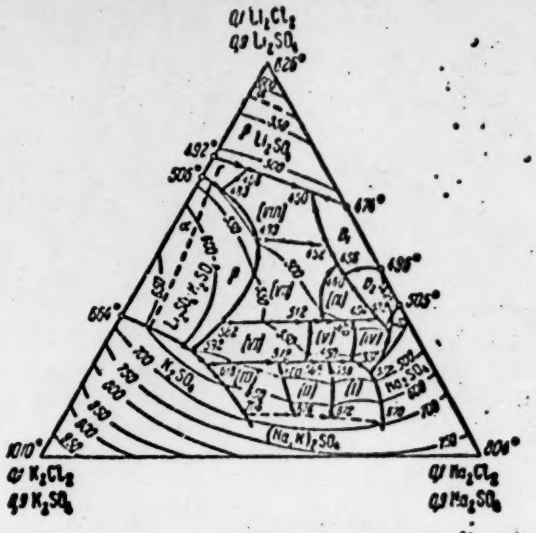

Fig. 4

In carrying out the complete investigation of this reciprocal quaternary system, we determined more than 8000 points, composition and crystallization temperature, not counting repeat determinations. The melting diagrams of 24 sections (triangular and square) through the prism were fully studied. Of these sections, the melting diagram of one vertical (inferior) section is shown in Figure 3, and that of a horizontal section is shown in Figure 4. Four phases -- [IX], [X], [XI], [XII], quaternary heterolonic compounds, were demonstrated by means of the internal sections of the system Li, Na, K ‖ Cl, SO_4.

The diagram of these sections shows that complex formation proceeds mainly in the interval of from 0 to 25-30 % chloride content.

25 volumes of crystallization were determined in the system Li, Na, K ‖ Cl, SO_4 ; polymorphic modifications were responsible for some of these. The experimental data and their graphical treatment established the presence of 46 non-variant quadruple points, of which 18 were eutectic points (Table 1). 139 univariant equilibrium curves of the 3 solid phases were established.

In conclusion, we may point out that the diagram is divided into 46 phase tetrahedra. This system is the most complex of all of the multicomponent salt systems which have been studied.

A more complete investigation of the equilibria of these six reciprocal salts in aqueous solution is desirable, and later a study of these salts over a broad temperature interval from the freezing points to various melt temperatures should be made in the hope of obtaining a complete picture of the effect of temperature and solvent on the chemism of the interaction of these components.

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A NEW ROUTE FOR THE SYNTHESIS OF STEROID COMPOUNDS

THE SYNTHESIS OF D-HOMOEQUILENIN AND D-HOMOISOEQUILENIN

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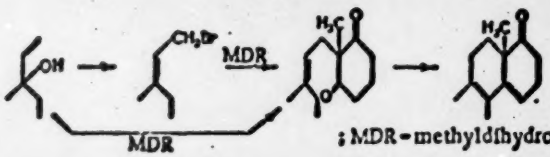
In one of our previous papers [1], we reported the synthesis of tri- and tetracyclic ketones by cyclization of disubstituted dihydroresorcinol, the reaction being carried out under the influence of phosphorus pentoxide.

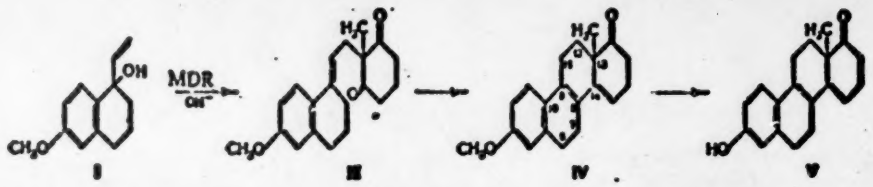


; MDR = methyldihydroresorcinol

The original diketones may be obtained both by alkylation of methyldihydroresorcinol [1] and by condensation of the latter with vinylcyclenols [2]; either the first or the second method may be the more suitable depending on the structure of the original carbinol.

We decided to apply this reaction to 1-vinyl-6-methoxyl-1-tetralol in order to synthesize a tetracyclic system with functional groups in the 3 and 17 positions, as in natural steroids.

Indeed, by heating 1-vinyl-6-methoxy-1-tetralol (I) with 1-methyldihydroresorcinol (II) in the presence of trimethylbenzylammonium hydroxide (triton B), we were able to prepare 3-methoxy-$\Delta^{1,3,5,9}$-8,4-seco-D-estratetraene-14,17a-dione (III) in 41% yield calculated on carbinol (I) and 60% calculated on the reacted diketone (II). Cyclization of diketone (III) with phosphorus pentoxide led to 3-methoxy-$\Delta^{1,3,5,8,14}$-D-homoestraenone (IV).



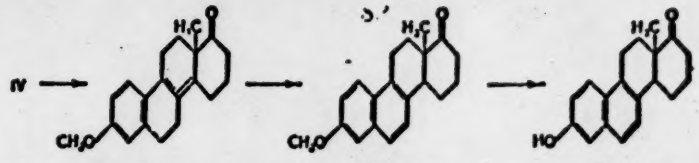
I III IV V

The structures of diketone (III) and ketone (IV) were confirmed by spectroscopic data and by the further conversions of these compounds.

Demethylation of ketone (IV) by heating it with pyridine hydrochloride produced the ketophenol (V). This same ketophenol (V) was formed by a similar treatment of diketone (III); i.e., the demethylation of the latter was accompanied by cyclization.

Hydrogenation of ketone (IV) in a mixture of alcohol and pyridine gave a difficultly separable mixture of trans-3-methoxy-$\Delta^{1,3,5,8}$-D-homoestratetraene-17a-one (VIa) and, apparently, its $\Delta^{8(14)}$-isomer (VIb). By analogy with the hydrogenation of 6,9-dimethyl-$\Delta^{4,8}$-hexahydronaphthalene-1-one (2b), which is similar in structure, the

addition of hydrogen to ketone (IV) should proceed from the least-shielded side in the 1,2 and 1,4 positions. This mixture, without being resolved, was subjected to dehydrogenation at 330° in the presence of palladium on carbon; this resulted in the formation of the methyl ethers of cis-D-homoequilenin (VIIa) and of trans-D-homoequilenin (VIIb). Cis-D-homoequilenin (VIIIa) and trans-D-homoequilenin (VIIIb) were obtained by demethylation of the two ketones.



The melting points of ketones (VIIb), (VIIIa), and (VIIIb) were in agreement with the literature values [3,4], but the melting point of ketone (VIIa) was higher by 50° than the value reported by Bachmann [3]. The u.v. spectra of ketones (VIIa) and (VIIb) were very close to the u.v. spectrum of β-methoxynaphthalene. Mixtures of D-homoequilenin (VIIIb) and of its methyl ether (VIIb) with known samples melted without depression of the melting points. These samples were kindly placed at our disposal by Prof. Chang Chin (Peking Petroleum Institute), for which we owe him our heartfelt appreciation.

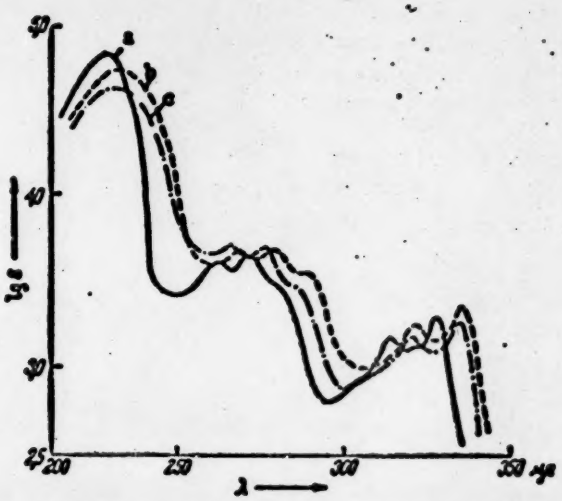


Fig. 1. U.v. spectra: a) β-methoxynaphthalene; b) methyl ether of trans-D-homoequilenin (VIIb); c) methyl ether of cis-D-homoequilenin (VIIa).

According to Bachmann, trans-D-homoequilenin (VIIIb) is active in doses of 50 γ as against 30 γ for equilenin when injected subcutaneously into mice.

EXPERIMENTAL PART

The 1-vinyl-6-methoxy-1-tetralol was prepared by the method previously described by us [5]. The methyldihydroresorcinol (II) was prepared by methylation of dihydroresorcinol.

Condensation of 1-vinyl-6-methoxy-1-tetralol (I) with methyldihydroresorcinol (II). A mixture of 10 g of carbinol (I), 6.2 g of methyldihydroresorcinol (II), triton B (from 1.3 g of the hydrochloride and 0.4 g of KOH in 3 ml of alcohol), and 12 ml of xylene was heated at 120-130° for 1 hour in a stream of nitrogen. The solution was cooled and diluted with 50 ml of ether, and the unreacted methyldihydroresorcinol (2.0 g) was separated. The ether solution was washed three times with a 5% solution of KOH and then with water, and was dried with

magnesium sulfate. After filtration and distillation of the solvent, the residue crystallized. There was obtained 6.2 g of diketone (III) with an m.p. of 89-90° (from alcohol); λ_{max} (in alcohol) 267 mμ (log ε 4.18); i. r. spectrum (in chloroform): 1720, 1694, 1601 cm^{-1}.

Found %: C 77.0, 76.7; H 7.8, 7.9; $C_{20}H_{24}O_3$. Calculated %: C 76.9; H 7.75.

Cyclization of diketone (III). A mixture of 12.7 g of diketone (III) and 1.2 g of phosphorus pentoxide was heated for 7 minutes at 120° and 95 mm. The reaction product was treated with soda solution and extracted with chloroform, and the extract was dried with magnesium sulfate. After filtration and distillation of the solvent, the residue crystallized completely. There was obtained 11 g of ketone (IV) with an m.p. of 135-136° (from alcohol); λ_{max} (in alcohol) 230, 308 mμ (log ε 3.18, 3.49). I.r. spectrum: 1699, 1598 cm^{-1}.

Found %: C 81.7; 81.5; H 7.45; 7.4. $C_{20}H_{22}O_3$. Calculated %: C 81.6; H 7.5.

2,4-Dinitrophenylhydrazone: m.p. 216-217° (from chloroform).

Found %: N 12.0; 12.0. $C_{26}H_{26}O_6N_4$. Calculated %: N 11.8.

Demethylation of diketone (III) and of ketone (IV). A mixture of 10 g of freshly prepared pyridine hydrochloride and 0.4 g of diketone (III) was heated in a stream of nitrogen at 210-215° for 40 minutes. When cool, the product was mixed with 200 ml of 5% hydrochloric acid and extracted with chloroform. The extract was agitated several times with 5% KOH solution, and the alkaline solution was acidified. There was obtained 0.23 g of $\Delta^{1,3,5,14}$-D-homoestrapentaen-3-ol-17a-one (V), m.p. 239-240° (of the solvate; from alcohol).

Found %: C 80.2; 80.3; H 7.2; 7.3. $4C_{19}H_{20}O_2 \cdot H_2O$. Calculated %: C 80.1; H 7.3.

The acetate, m.p. 149-150°, was obtained by heating ketophenol (V) with acetic anhydride in pyridine (100°, 3 hour). The demethylation of ketone (IV) was carried out in a similar manner. From 1 g of ketone (IV) was obtained 0.2 g of ketophenol (V) with an m.p. of 239-240°; a mixture of this compound with the sample prepared above showed no depression of the melting point.

Hydrogenation of ketone (IV). 1 g of ketone (IV) in a mixture of 15 ml of alcohol and 10 ml of pyridine was hydrogenated in the presence of 5% palladium on calcium carbonate. The hydrogenation proceeded rapidly, and after 10 minutes, 84 ml of hydrogen had been absorbed; this amount may be compared with the 77 ml theoretically required, calculated for one double bond. There was obtained 0.74 g of a mixture of ketones (VIa) and (VIb) with an m.p. of 124-127°; we were unable to resolve this mixture by crystallization. λ_{max} (from alcohol) 276 mμ (log ε 4.21).

Found %: C 80.8; 81.1; H 8.3; 8.3. $C_{20}H_{24}O_2$. Calculated %: C 81.0; H 8.2.

Similar results were obtained by hydrogenation of ketone (IV) in benzene in the presence of palladium on carbon and platinum in ethyl acetate.

Dehydrogenation of the mixture of cis-and trans-ketones (VIa and VIb). 2.36 g of the mixture of ketones (VIa) and (VIb) and 1.2 g of 15% palladium on carbon were heated at 320-330° for 10 minutes, during which 180 ml of gas ml of gas evolved (primarily hydrogen). When cool, the mixture was extracted with 200 ml of boiling chloroform. The extract was filtered and evaporated, and the residue was crystallized from ethyl acetate. There was obtained 0.4 g of the methyl ether of D-homoequilenin (VIIb), m.p. 214-215°, and 0.4 g of its cis isomer (VIIa), m.p. 175-176°.

For ketone (VIIb): λmax (in alcohol) 229.5, 267.5, 278, 288.5, 336 mμ (log ε 4.73, 3.69, 3.72, 3.56, 3.28, 3.36).

Found %: C 81.35, 81.4; H 7.7, 7.7; $C_{20}H_{22}O_2$. Calculated %: C 81.6; H 7.5.

The semicarbazone had an m.p. of 243-245°. Bachmann gives for ketone (VIIb) an m.p. of 213-214° and for the semicarbazone an m.p. of 244-246°. For ketone (VIIa) λ_{max} (in alcohol): 228.6, 266, 276, 286, 319, and 335 mμ (log ε 4.64, 3.68, 3.47, 3.20, and 3.30).

Found %: C 81.55, 81.8; H 7.7, 7.7; $C_{20}H_{22}O_2$. Calculated %: C 81.6; H 7.5.

Bachmann gives an m.p. of 125-126° for ketone (VIIa) [3]. For β-methoxynaphthalene λ_{max} (in alcohol): 227, 261.5, 271, 314, and 328 mμ (log ε 4.85, 3.61, 3.65, 3.19, 3.30).

A mixture of a sample of the methyl ether of D-homoequilenin (VIIb) with the sample provided by Prof. Chang Chin [4] showed no depression of the melting point.

Demethylation of ketones (VIIa) and (VIIb) to cis- and trans-D-homoequilenins (VIIIa) and (VIIIb). A mixture of 158 mg of ketone (VIIa), 25 ml of glacial acetic acid, and 8 ml of 48 % hydrobromic acid was refluxed for 1 hour in a stream of nitrogen. After the solution had cooled, it was poured in 30 ml of water, and the precipitate was filtered and dissolved in 75 ml of 5% KOH. The alkaline solution was filtered, acidified with hydrochloric acid, and extracted with ether. From the extract, after evaporation and crystallization, was obtained 83 mg of cis-D-homoequilenin (VIIIa) with an m.p. of 244-245° (from alcohol); λ_{max} (in alcohol) 228, 267.5, 278, 289, 324.5, and 338 mμ (log ε 4.81, 3.75, 3.58, 3.33, 3.39). See Figure 3 for the i.r. spectrum.

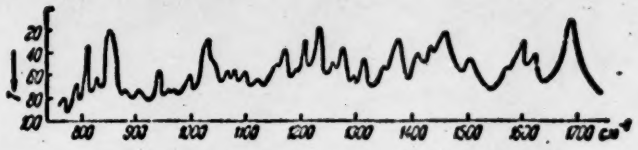


Fig. 2. I.r. spectrum of trans-D-homoequilenin (VIIIb).

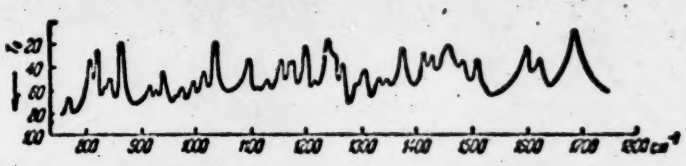


Fig. 3. I.r. spectrum of cis-D-homoequilenin (VIIIa).

Similarly, from 200 mg of ketone (VIIb) was obtained 50 mg of D-homoequilenin (VIIIb) with an m.p. of 234-235° (from alcohol); λ_{max} (in alcohol): 230, 270, 281, 292, 326, and 339 mμ (log ε 4.80, 3.68, 3.74, 3.59, 3.33, and 3.39). See Figure 2 for the i.r. spectrum. Bachmann gives 239-240° for the m.p. of the cis-isomer (VIIIa) and 232-233° for the m.p. of the trans isomer (VIIIb) [3]. A mixture of a sample of D-homoequilenin (VIIIb) with a sample of the material provided by Prof. Chang Chin [4] melted without depression of the melting point.

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CONFIGURATIONAL RELATIONSHIPS DURING STEREOSPECIFIC CATALYSIS

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The multiplet theory of catalysis points out the necessity for the existence of a structural correspondance between the reacting molecule and the fine structure of the catalyst surface. This correspondence has been studied for a number of cases of heterogeneous catalysis [1-3]. Inasmuch as the principles of structural and energetic correspondence required by the multiplet theory have also been applied to enzyme catalysis [4-6], it became necessary to trace these correspondences in the field of asymmetric microheterogeneous catalysis. Such reactions are of considerable interest in catalysis theory, since in this case the substituents along the boundary in the reaction index exert a particularly strong effect. In this case, the effectiveness of stereospecific catalysis depends on the degree of structural correspondence. In this connection, extension of our knowledge concerning reactions catalyzable by microheterogeneous asymmetric catalysts — models of enzymes — is of great interest.

Skita's catalyst – colloidal platinum or palladium with gum arabic as a protective colloid – was selected as such a catalyst. This catalyst has been used for the hydrogenation of a number of compounds containing multiple bonds, including compounds which, upon hydrogenation, yield products with an asymmetric carbon atom (for example, the catalyst has been used for the preparation of ephedrine derivatives [7]). However, for various reasons the appearance of optical activity in the reaction products has not been noted, up to the present, when such colloidal catalysts are used (the reasons for this include possible racemization, low specific rotation of the reaction product, etc.). Moreover, as we have been able to clarify [8], such a catalyst displays stereospecificity of action, though it may not be high.

The platinum and palladium catalysts were prepared by the method of Skita [9] as modified by Karyakin [10]. The gum arabic solution used had $[\alpha]_D^{20} = -26°$. The asymmetric reactions selected for this study comprised hydrogenation of C=O and C=N bonds in keto acids and in a dioxime. The amounts of the starting compounds were selected so that during the optical measurements even a small optical rotation of the product of the asymmetric synthesis could be detected, providing, of course, that asymmetric synthesis occurred. As examples of such compounds, we used phenyl- and α-naphthylglyoxylic acids, which yield hydroxy acids with high specific rotations: mandelic acid with $[\alpha]_D^{20} = -157°$ and α-naphthylglycolic acid with $[\alpha]_D^{20} = +230°$. It should be pointed out that these two acids, which rotate polarized light in opposite directions, belong to one configurational series. In addition, we investigated the hydrogenation of N,N'-diacetyldiphenylglyoxime to diphenylethylenediamine, the specific rotation of which changes within wide limits depending on the concentration of the solution investigated.

The phenylglyoxylic acid (m.p. 73°) and the α-naphthylglyoxylic acid (m.p. 104-105°) were prepared by oxidation of, respectively, acetophenone and α-naphthyl methyl ketone with alkaline permanganate at 0°. The keto acids were purified with carbon disulfide and recrystallized from CCl_4 [11]. The N, N'-diacetyldiphenylglyoxime (m.p. 146-147°) was prepared by oximization of benzil with subsequent acetylation. The hydrogenation was carried out in a thermostated catalytic bomb at 600-700 oscillations per minute, atmospheric pressure, and a temperature of 20-40°; dioxane, acetic acid, or water was used as the solvent. Inasmuch as palladium catalysts are several times more active than platinum catalysts, 20 ml of the colloidal solution of catalyst containing 0.12 g of platinum and 0.2 g of protective colloid was used in each experiment with the platinum catalysts; in the case

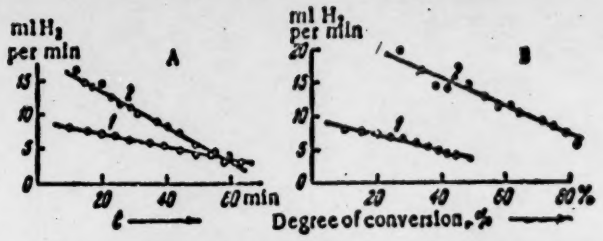

Fig. 1. Hydrogenation of phenylglyoxylic acid (1) and of N,N'-diacetyldiphenylglyoxime (2) as functions of time (A) and of degree of conversion (B).

of the palladium catalyst, 5 ml of solution containing 0.03 g of palladium and 0.10 g of gum arabic was used. The calculated amount of hydrogen was absorbed in all hydrogenations. In Figure 1 are shown the kinetic curves, plotted as rate vs. time and rate vs. degree of conversion, for the hydrogenation of phenylglyoxylic acid and the dioxime.

At the conclusion of the reaction, the catalyst was coagulated by acidification of the solution and subsequent heating, or it was separated by extraction of the product with ether. During isolation of the reaction products, particular attention was paid to their separation from traces of the levorotatory colloid in the form of crystallizable derivatives. Mandelic and α-naphthylglycolic acids were separated through their copper, silver, or barium salts. The mandelic acid obtained had an m.p. of 117.5-118.5° (a mixed sample showed no melting point depression); the α-naphthylglycolic acid had an m.p. of 95° (with decomposition). The diamine was separated through the hydrochloride and carbamate (m.p. 106-107°); the base was investigated polarimetrically.

Optical activity was measured with a "Bellingham" half-shade polarimeter using light from a sodium lamp; the accuracy of the reading was 0.01°, and the average error of the measurements was 0.003-0.005°. The percentage content of the optically active product, P(%), was determined from the ratio of the specific rotation of the reaction product to the specific rotation of the optically pure compound. The results of the most characteristic experiments are presented in Table 1.

The comparatively high value of the specific rotation of the diamine product merits attention during a consideration of the data presented in the table.

The data obtained make it possible to detect a definite configurational relationship between the catalyst and the reacting molecules. First of all, it is necessary to point out that in the cases investigated, the protective colloid (gum arabic) apparently served as an asymmetric carrier, and not as an optically active solvent. Otherwise, the catalyst undergoing coagulation during the reaction (as a result of an increase in temperature or when an unsuitable solvent was used) would not have lost its stereospecific action. Under the influence of the asymmetric structure of the carrier - gum arabic, which consists chiefly of residues of L-arabinose - during the hydrogenation of benzoylformic acid there was formed a small excess of the natural levorotatory mandelic acid, which has a D configuration. The dextrorotatory α-naphthylglycolic acid obtained also belongs to the D series. This indicates that during catalysis, our asymmetric carrier acts selectively, promoting predominantly the formation of acids with a D configuration. The configuration of the optically active diphenylethylenediamine product, the structure of which presumes the presence of asymmetry of the type of tartaric acid, must also correspond to the structure of the carrier. Consequently, on the basis of the sign of the rotation (the dextrorotatory diamine is formed), the diamine must also belong to the D series. However, this conclusion cannot be considered a final one, since, as Akabori and co-workers found [12], a dextrorotatory diamine is formed during asymmetric hydrogenation of diphenylglyoxime over a catalyst of palladium on silk, and, under the conditions investigated, the formation of amino acids of the L series (glutamic acid, phenylalanine) was observed during the hydrogenation of the corresponding imino compounds.

Our data confirm the presence of a close configurational correspondence between the asymmetric catalyst (more precisely, an asymmetric carrier) and the steric structure of the reacting molecule. The necessity of such correspondence, which must be considered a basic condition of asymmetric synthesis, was pointed out during a consideration of the mechanism of asymmetric catalysis using catalysts based on optically active quartz [13].

TABLE 1

Optically active product	Catalyst	α_D^{20} (l = 1.9009)	Concn., g per 100 cc	Solvent	$[\alpha]_D^{20}$	P (%)	Configurational series
Mandelic acid	Pd	−0.071°	5.0	CH_3COOH	−0.74	0.4	D
		−0.052°	4.0	CH_3COOH	−0.68	0.42	D
α-Naphthylglycolic acid	Pd	+0.03°	1.2	CH_3COOH	+1.2	0.8	D
N,N'-Diacetyldiphenylethylenediamine	Pt	+0.074°	0.32	$C_2H_5OC_2H_5$	+12.5		
	Pt	+0.65° (l=4)	0.38	$C_2H_5OC_2H_5$	+42.7		D (7)
N,N'-Diacetyldiphenylethylenediamine·2HCl	Pd	+0.05°	1.4	H_2O	+1.8		

In the present case, the protective colloid served not only as a stabilizer for the metal sol, but also as an asymmetric carrier; this is confirmed by the fact that asymmetric synthesis of hydroxy acids and of a diamine occurred when a catalyst with a protective colloid was used. This point of view was also confirmed by special experiments which showed that the reaction product (mandelic acid) has no optical activity when the hydrogenation of phenylglyoxylic acid is carried out in a solution of gum arabic with a catalyst of palladium on silica gel. As the work of Bredig, Voegler, Cohen, and Rice and others [2] has shown, an asymmetrizing effect on the reaction by an optically active solvent sometimes appears, although to a slight extent. That this was not observed in the present case indicates the small asymmetrizing actionby the polysaccharide – gum arabic solution used. This is observed in a catalytic reaction when the colloid is simultaneously the carrier. Finally, the data obtained permit expansion of our concept of the nature of the colloidal catalyst, and they show that the metal particle is not in the solvated film of the micelle, but is in direct contact with the asymmetric molecules of the protective colloid, owing to which the occurrence of asymmetric adsorption and asymmetric catalysis becomes possible.

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ENTHALPIES OF POLYMERIZATION OF N-SUBSTITUTED LACTAMS

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(Presented by Academician A. A. Balandin, April 4, 1959)

Generalizations for polymerization processes of heterocyclic compounds cannot be established without the systematic accumulation of material in this field. A number of authors [1,2] have asserted that the differences in the abilities of different heterocyclic compounds within a given homologous series to undergo polymerization under the same conditions can be explained only by the change in enthalpy and entropy during these reactions. However, until recently there has been no experimental data which would permit quantitative consideration of this question, even for one series of heterocyclic compounds.

The change in enthalpy for a polymerization reaction can be found comparatively readily as the difference between the heat of combustion of the monomer and that of the polymer unit (the latter can, in many cases, be reliably calculated). Dealing with entropies is considerably more complex. There are almost no experimental data for corresponding substances, and attempts to calculate these values do not always yield reliable results. In a series of papers [1,2] we assumed, and Dainton and co-authors showed on the basis of a considerable amount of material [3], that the change in the thermodynamic potential during polymerization of carbocyclic compounds (with 5- to 8-membered rings) is determined chiefly by the change in enthalpy (ΔH); the entropy change in these reactions is comparatively small. It has recently been experimentally determined that the entropy change during the polymerization of ϵ-caprolactam is small [4]. Thus, even in the absence of entropy data, the investigation of the heats of combustion of corresponding substances and the calculation from these data of the enthalpy change during a polymerization reaction (hypothetical in some cases) has significance.

In previous work, we evaluated ΔH for the polymerization of lactams with 5 to 8 atoms in the ring. It is well known that a substituent, even at a carbon atom, reduces the ability of a compound to undergo polymerization [5]. The polymerization of amides with a substituent on the nitrogen atom is still more difficult. It has even been asserted that N-substituted lactams generally are incapable of polymerization [6]. Since it has been established that N-methylenantholactam does polymerize [7], it appeared to be of interest to obtain data which would permit evaluation of ΔH for the polymerization of methyl-substituted lactams with from 5 to 8 atoms in the ring.

The present article reports the results of determinations of the heat of combustion of N-methylpyrrolidone, N-methylpiperidone, N-methylcaprolactam, N-methylenantholactam, and N-ethyl-N-methylpropionamide (the heat of combustion of the latter substance was used in the calculations). All of these substances were synthesized and carefully purified by fractional distillation at reduced pressure in a stream of nitrogen*. These substances, contained in thin-walled glass ampoules, were burned in a calorimetric bomb. In order to exclude contact of the substances with moist air, filling of the ampoules was accomplished during the distillation (in a stream of dry nitrogen). The methods used for measuring the heats of combustion have been described previously [8]. The amount of material burned in each experiment was determined from the amount of carbon dioxide found during analysis of the combustion products (absorption of CO_2 by ascarite). This method of analysis was developed during a series of experiments in which a standard, benzoic acid, was burned, and it permits determination of CO_2 with a total amount of CO_2 of about one gram with an accuracy of ($\pm 0.02\%$). The close agreement between the amount

* The synthesis and purification of the substances were carried out in the Institute of Synthetic Fibers by N. F. Erofeeva.

TABLE 1

Compound, in the liquid state	n_D^{25}	d_4^{25}	$-\Delta H_c^{25}$ kcal/mole	CO_2 found / CO_2 calc.
N-CH_3-pyrrolidone	1,4670	1,0252	715,0±0,1	1,0015
N-CH_3-piperidone	1,4801	1,0271	870,0±0,1	1,0000
N-CH_3-caprolactam	1,4809	1,0115	1029,1±0,1	1,0005
N-CH_3-enantholactam	1,4880	1,0103	1187±0,3	0,9999
N-Ethyl-N-methyl-propionamide	1,4400*	1,9075*	928,1±0,1	1,0004

* At 20°.

of carbon dioxide found in the combustion products (CO_2 found) and that calculated from the original sample weight (CO_2 calc.) served as a criterion of the completeness of combustion and of the purity of the preparation.

The physicochemical constants of the substances investigated and the experimental data are presented in Table 1.

In column 4 are shown the changes in enthalpy, in kcal / mole (cal = 4.1840 abs. joules), during isothermal combustion (25°) of the substances in the liquid state at a pressure of 1 atm, the reaction products being gaseous CO_2 and N_2 and liquid water at a pressure of 1 atm. From these values, heats of polymerization (ΔH_p, for the liquid state) for all of the lactams investigated were calculated according to the schemes

$\Delta H_p = \Delta H'_c$ monomer $- \Delta H''_c$ polymer unit in the linear molecule.

$$CH_3 - N(CH_2)_nCO \qquad -\underset{\displaystyle CH_3}{\underset{|}{N}}(CH_2)_nCO-$$

$\Delta H'' = 156,3p + 245,3$ kcal., where p is the number of CH_2 groups, and the value 156,3 kcal is the increment in the heat of combustion per CH_2 group [10]. The increment for the $-\underset{\displaystyle CH_3}{\underset{|}{N}}-CO-$ group was taken as the difference between the observed heat of combustion of N-ethyl-N-methylpropionamide and the known heat of combustion of n-butane [10]; it was found to be 245,3 kcal.

It is interesting to compare the values of ΔH_p for N-substituted lactams with values of ΔH_p determined by us previously by a similar calculation for unsubstituted lactams with the same number of atoms in the ring (Table 2).

As may be seen from these data, N-methyl-substituted lactams have lower heats of polymerization than the unsubstituted lactams with the same number of atoms in the ring. This has very recently been noted by Jumoto and co-authors during a study of the effect of side chains on the polymerization of ε-caprolactam [11]. Of the compounds investigated, the highest heat of polymerization (3,9 kcal / mole) was found for the eight-membered N-methylenantholactam; it agreed with the value for the heat of polymerization of ε-caprolactam. Thus, in both series of compounds, those compounds for which the heat of polymerization is less than 3,8 kcal per mole do not polymerize under the conditions indicated in the table.

TABLE 2

No. atoms in the ring	N-CH_3-substuted lactams		Lactams	
	ΔH_p^{25} kcal/mole	Ability to polymerize*	ΔH_p^{25} Kcal/mole	Ability to polymerize*
5	0,8	No polymeriz.	1,1	No polymeriz.
6	−0,5	" "	2,2	" "
7	2,3	" "	3,8	Polymerized
8	3,9	Polymerized	5,3	"

* Polymerization by heating to 200-249° with a small amount of activator and at a pressure of 1 atm.

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A NEW METHOD FOR THE PREPARATION OF PROPIOTHIOLACTONES

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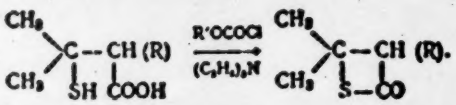
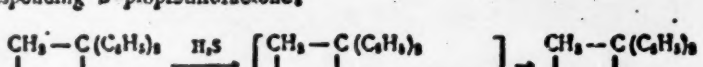
We have previously shown that β-mercapto acids yield β-propiothiolactones under the influence of ethyl chlorocarbonate in the presence of triethylamine [1-3].

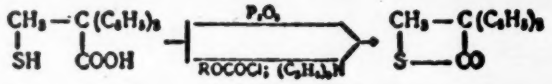


It has now been found that these same thiolactones can be successfully obtained by the action of hydrogen sulfide on the chlorides of β-halocarboxylic acids. This method compares favorably with that previously described in that it does not require the special preparation of difficultly available β-mercapto acids, and also in the requirement for separating the intermediately formed β-halothiolcarboxylic acids. Thus, the action of hydrogen sulfide on β-chloro and β-bromo-α,α-diphenylpropionyl chloride in methylene chloride solution in the presence of triethylamine gave α,α-diphenyl-β-propiothiolactone (I) in a yield of above 90%. It seems natural that the first stage of the reaction is the formation of triethylammonium-β-halo-α,α-diphenylthiolcarboxylate, which then readily cyclizes to the corresponding β-propiothiolactone:



Extension of this reaction to the chlorides of other β-halocarboxylic acids showed that this new method is a general method for the preparation of β-propiothiolactones. Thus, from α-methyl-α-ethylthio-β-chloropropionyl chloride and β,β-dimethyl-β-bromopropionyl chloride were obtained, respectively, α-methyl-α-ethylthio-β-propiothiolactone and the previously described β,β-dimethyl-β-propiothiolactone. More careful investigation of the conditions of formation of β-propiothiolactones by the new method showed that, depending on the stability of the β-propiothiolactone formed, in certain cases sodium sulfide can be used in place of hydrogen sulfide. In order to avoid cleavage of the resulting thiolactone with the formation of a β-mercaptothiolcarboxylic acid during the preparation, a low temperature should be maintained, the theoretical amount of triethylamine should be used, and an excess of hydrogen sulfide should be avoided.

During this investigation, it was also found possible to prepare α,α-diphenyl-β-propiothiolactone by anhydridization of α,α-diphenyl-β-mercaptopropionic acid, both by the action of ethyl chlorocarbonate and by the action of phosphorus pentachlorides:



It is interesting to note that, in contrast to the anhydridization of β-mercapto acids, anhydridization of β-hydroxy acids proceeds primarily with the formation of α, β-unsaturated carboxylic acids. In the case of α,α-disubstituted β-hydroxy acids also, β-propiolactones are not formed, and a reverse of the aldol condensation occurs [4,5]:

$$RCH(OH)-C(R')_2(COOH) \rightarrow RCHO + R'_2CHCOOH.$$

An exception in this series is β,β-di(trifluoromethyl)-β-hydroxypropionic acid, the anhydridization of which in our laboratory recently led to β,β-di(trifluoromethyl)-β-propiolactone.

EXPERIMENTAL PART

α,α-Diphenyl-β-propiothiolactone (I). a) To 2.2 g (0.0089 mole) of α,α-diphenyl-β-mercaptopropionic acid in 50 ml of chloroform at -10° was added 0.5 ml (0.0107 mole) of triethylamine followed by 0.9 ml (0.009 mole) of ethyl chlorocarbonate in 20 ml of chloroform. The mixture was allowed to stand for 1 hour at -10°, the triethylamine hydrochloride was precipitated with absolute ether (200 ml), and the mixture was allowed to stand at room temperature until the following day. The triethylamine hydrochloride was filtered, the filtrate was washed with magnesium sulfate, and the solvent was distilled under vacuum at room temperature. The residue was crystallized from heptane. The yield was 1.5 g (70%); m.p. 55-56°. The colorless needles were readily soluble in ether, benzene, and chloroform, difficultly soluble in heptane, and insoluble in water.

Found %: C 74.90; H 5.25; S 12.46. $C_{15}H_{12}OS$. Calculated %: C 75.00; H 5.00; S 13.33.

Cleavage of I with 10% aqueous alcoholic alkali (1:1) (3 hours at ~ 100°) gave α,α-diphenyl-β-mercaptopropionic acid (85 %), m.p. 197-199° (m.p. from the literature [6], 200-202.5°). A mixed sample with known α,α-diphenyl-β-mercaptopropionic acid melted without depression of the melting point.

b) 0.8 g (0.003 mole) of powdered α,α-diphenyl-β-mercaptopropionic acid was mixed with 1.25 g (0.008 mole) of phosphorus pentoxide and heated for 6 hours on a boiling water bath, and the mixture was then extracted with hot petroleum ether. 0.45 g (62%) of I was obtained. The yield did not change when the preparation was carried out in solution in meta xylene.

c) To a solution of 3.23 g (0.01 mole) of α,α-diphenyl-β-bromopropionyl chloride in 35 ml of methylene chloride was added dropwise a solution of 2.64 g (0.011 mole) of $Na_2S \cdot 9H_2O$ in 35 ml of alcohol. The mixture was evaporated to dryness under vacuum, the residue was extracted with ether, and the ether solution was washed with water and dried with magnesium sulfate. Evaporation of the ether gave I in quantitative yield.

d) 3.23 g (0.01 mole) of α,α-diphenyl-β-bromopropionyl chloride (or the corresponding amount of α,α-diphenyl-β-chloropropionyl chloride) was dissolved in 30 ml of methylene chloride, and the solution was saturated with hydrogen sulfide at -10° for 1 hour. 2.8 ml (0.02 mole) of triethylamine in 5 ml of methylene chloride and 5 ml of absolute ether were added dropwise to the solution over a period of 30 minutes and during the addition the mixture was saturated with hydrogen sulfide. The temperature was raised to room temperature, and 100 ml of absolute ether was added. After removal of the precipitated triethylamine hydrochloride and hydrobromide, the solution was washed with water and dried with magnesium sulfate. The solvent was evaporated. There was obtained 2.3 g (96%) of I. If after the addition of the triethylamine was complete, hydrogen sulfide was passed into the reaction mixture for an additional 10 hours, the yield of I did not exceed 40%, and 1.8 g (16%) of triethylammonium α,α-diphenyl-β-mercaptothiolpropionate, m.p. 107-108° (from alcohol), was obtained as a by-product.

Found %: C 66.78; H 7.89; N 4.09; S 16.67. $C_{21}H_{29}NOS_2$. Calculated %: C 67.20; H 7.73; N 3.73; S 17.08.

α-Methyl-α-ethylthio-β-propiothiolactone (II). 50 ml of CH_2Cl_2 was saturated at -10° with hydrogen sulfide for 30 minutes; 9.12 g (0.05 mole) of α-methyl-α-ethylthio-β-chloropropionyl chloride in 25 ml of absolute ether and then 10.1 g (0.1 mole) of triethylamine were added dropwise while hydrogen sulfide was passed into the reaction mixture, and the addition of H_2S was continued for another 10 minutes. After 1.5 hours, absolute ether was added until the precipitation of triethylamine hydrochloride was complete, the mixture was filtered, and the filtrate was washed with water and dried with magnesium sulfate. Evaporation of the solvent gave 4 g, 50 % yield, of α-methyl-α-ethylthio-β-propiolactone as a light yellowish liquid; b.p. 68-70°/0.1 mm; n_D^{20} 1.5425. MR: found, 44.21; calculated 43.67. Mol. wt. (cryoscopic, in benzene) 156. Density 1.154.

Found %: C 43.55; H 6.29; S 39.07. $C_6H_{10}OS_2$. Calculated %: C 44.4; H 6.17; S 38.27.

Cleavage of II with aqueous-alcoholic hydrochloric acid (1:1) (3 hours, ~100°) gave α-methyl-α-ethylthio-β-mercaptopropionic acid, b.p. 140-143°/1-2 mm. Similarly, from β,β-dimethyl-β-bromopropionyl chloride was obtained a 46% yield of β,β-dimethyl-β-propiothiolactone, b.p. 33-34°/1-2 mm.

Benzyl-α-methyl-α-ethylthio-β-mercaptopropionamide. To 1.62 g (0.01 mole) of α-methyl-α-ethylthio-β-propiothiolactone in 25 ml of absolute ether was added 1.07 g (0.01 mole) of benzylamine in 25 ml of absolute ether. The mixture was allowed to stand at room temperature in a sealed flask without access of air until the following day, and the benzylamide was then extracted from the ether solution with 1 N NaOH. Acidification of the aqueous solution with 2 N H_2SO_4 gave benzyl-α-methyl-α-ethylthio-β-mercaptopropionamide in quantitative yield; m.p. 60-61° (from petroleum ether).

Found %: C 57.18; H 7.16; 23.56*. $C_{13}H_{19}OS_2N$. Calculated %: C 58.00; H 7.06; 23.78*.

The benzyl-α-methyl-α-ethylthio-β-mercaptopropionamide readily oxidized in air to the corresponding disulfide, m.p. 121° (from absolute alcohol).

Found %: C 58.07; H 6.90; S 24.01. $(C_{13}H_{19}OS_2N)_2$. Calculated %: C 58.20; H 6.71; S 23.90.

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* As in the original. The number probably gives the value of S.

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CATALYTIC ISOMERIZATION OF HYDROCARBONS OF THE CYCLOBUTANE SERIES

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Until recently, only a small amount of work had been reported on the isomerization of hydrocarbons of the cyclobutane series. Thus, V. N. Ipatieff and N. L. Tikhotskii [1] carried out experiments on the isomerization of methylcyclobutane under the influence of clay at 290-300°, and they found that opening of the four-membered ring occurred under the conditions of the experiments. O. Filipov [2] reported that when methylenecyclobutane is passed over aluminum oxide at 300°, almost complete isomerization to methylcyclobutene takes place. At higher temperatures (400-430°) according to the data of Doyarenko [3], isoprene is obtained from methylenecyclobutane in the presence of aluminum oxide.

The isomerization of methylcyclobutane under the influence of aluminum oxide and thorium oxide was studied by N. A. Rozanov [4], and, judging from the boiling range of the catalyzate, a mixture of 2-pentene, 2-methyl-1-butene, and 3-methyl-1-butene was obtained. M. B. Turova-Polyak and M. Yu. Lukina [5] studied the isomerization of ethylcyclobutane under the influence of aluminum chloride, and these investigators established that this reaction results in the formation of methylcyclopentane and cyclohexane. More recently, V. N. Ipatieff and co-workers [6] studied the behavior of methyl-, ethyl- and isopropylcyclobutane in the presence of aluminum chloride, and they found that methylcyclobutane polymerizes, while ethyl- and isopropylcyclobutanes isomerize with expansion of the ring to five and six members.

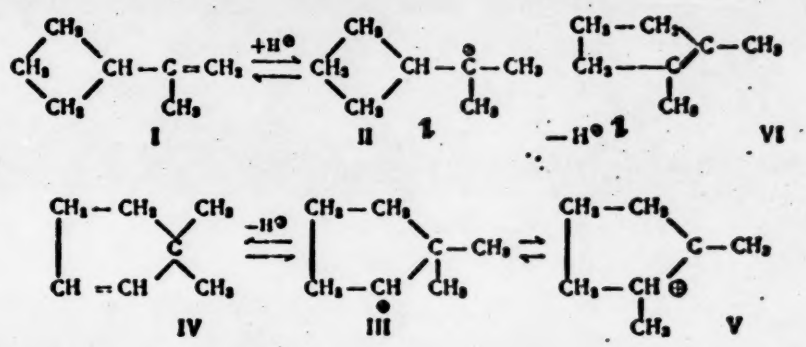
The work described above does not exhaust the possibilities with respect to either the conditions required for isomerization of the four-membered ring or the reaction products, and this prompted us to begin a systematic investigation in this field.

We decided to investigate the behavior of hydrocarbons of the cyclobutane series in the presence of catalysts which cause isomerization of a three-membered ring, using conditions which would permit a comparison of the stability of three- and four- membered rings. We early encountered an interesting phenomenon: under conditions for chromatographic adsorption on silica gel, alkylcyclobutanes [7], in contrast to alkylcyclopropanes [8], do not undergo isomerization; however, isopropenylcyclobutane isomerized under these conditions with expansion of the rings to five members [9]. Thus, the behavior of alkylcyclobutanes on silica gel differs sharply from the behavior of alkenylcyclobutane, which proved to be even less stable than alkylcyclopropanes. In connection with this observation, the present work was devoted to a study of the behavior of saturated hydrocarbons—ethyl- and isopropylcyclobutane—and unsaturated hydrocarbons of this same series having the double bond in different positions in the substituent: isopropenyl- and isopropylidenecyclobutane, in the presence of catalysts which have, like silica gel, an acid nature.

It was found that aluminosilicate, which completely isomerizes alkylcyclopropanes at 50° [10], did not cause appreciable isomerization of isopropylcyclobutane even at 250°. Kieselguhr, which completely isomerizes alkylcyclopropanes at 150° [10], caused no change in alkylcyclobutanes at 150°, 200°, 300°, or 400°; only at 500° was there obtained a catalyzate which differed sharply in physical constants from the original hydrocarbon, and this could be attributed to the effect of the high temperature. Thus, it was shown that alkylcyclobutanes, in distinction to alkylcyclopropanes, are quite stable compounds under isomerization conditions.

Unsaturated hydrocarbons of the cyclobutane series behaved completely differently. Thus, isopropenylcyclobutane completely isomerized with expansion of the ring to five members in the presence of Kieselguhr at 200°. On the basis of the Raman spectrum, the hydrogenated isomerizate consisted of a mixture of 1,2-dimethylcyclopentanes with traces of 1,1-dimethylcyclopentane.

When passed through kieiselguhr under these same conditions, isopropylidenecyclobutane gave an isomerizate possessing the same properties and, consequently, having the same composition as the isomerizate obtained with isopropenylcyclobutane. This was confirmed in an experiment with silica gel; a catalyzate having the same composition as the catalyzate from isopropenylcyclobutane [9] was obtained by filtration of isopropylidenecyclobutane through silica gel. In this manner it was shown that, regardless of the position of the double bond in the substituent, unsaturated hydrocarbons of the cyclobutane series readily undergo isomerization yielding the same reaction products, and they isomerize under conditions under which alkylcyclobutanes are not changed. It should be pointed out at this time that all of the catalysts investigated are capable of causing double-bond shifting; therefore, it is possible that isomerization of the ring is preceded by a double-bond shift, and in both cases (isopropenyl- and isopropylidenecyclobutane) the same unsaturated hydrocarbon reacted. Considering that according to contemporary ideas isomerization reactions in the presence of acid catalysts proceed by a carbonium ion mechanism [11], the conversion of isopropenylcyclobutane can be represented as follows:



As a result of the addition of a proton from the catalyst to I, carbonium ion II is formed; this is a polar compound $R^+ A^-$, where A^- is the anion of the acid catalyst. II then rearranges to III (with expansion of the ring), and then either stabilization occurs by loss of a proton with the formation of IV, or migration of a methyl group III ⇄ V first occurs with subsequent stabilization by loss of a proton with the formation of VI. This mechanism explains the presence in the isomerization product of isopropenylcyclobutane of both 1,1-dimethylcyclopentane and 1,2-dimethylcyclopentanes. It also becomes clear why saturated hydrocarbons of the cyclobutane series either undergo practically no isomerization or else isomerize with great difficulty under these conditions.

EXPERIMENTAL PART

The hydrocarbons required to carry out the present investigations were synthesized by a previously described method [5,7]. Their constants are presented in Table 1. The experiments on isomerization in the presence of aluminosilicate and kieselguhr were carried out in the vapor phase. The amount of catalyst in all experiments was 10 ml (3.0 g), and the space rate was 0.2 hours^{-1}. The unsaturated catalyzates were hydrogenated in the liquid phase; the hydrocarbons were separated, dried, and distilled.

Study of the ethylcyclobutane behavior in the presence of kieselguhr. Ethylcyclobutane (about 2.5 g in each experiment) was passed over the catalyst at various temperatures. The catalyzates obtained at 200°, 300°, and 400° had n_D^{20} 1.4020 and d_4^{20} 0.7265, which are characteristic of unchanged ethylcyclobutane. The catalyzate obtained at 500° had n_D^{20} 1.3898, d_4^{20} 0.6826, instantly decolorized bromine water and had a bromine number of 101.

Study of the behavior of isopropylcyclobutane in the presence of aluminosilicate. Isopropylcyclobutanes in portions of 2.0–4.0 g, was passed over the catalyst at 200°, 225°, and 250°. In all cases, the catalyzates were only slightly different from the original hydrocarbon in index of refraction. 9.3 g of catalyzate from all experiments

TABLE 1

Hydrocarbon	B.p., deg C at 760 mm	n_D^{20}	d_4^{20}
Ethylcyclobutane	70,4	1,4020	0,7269
Isopropylcyclobutane	92,5	1,4082	0,7380
Isopropenylcyclobutane	98,7	1,4347	0,7743
Isopropylidenecyclobutane	107,3	1,4458	0,7825

had n_D^{20} 1.4086; d_4^{20} 0.7390. According to the Raman spectrum, the catalyzate was unchanged isopropylcyclobutane and contained only traces of 1,2-dimethylcyclopentane *.

Isomerization of isopropenyl- and isopropylidenecyclobutane on kieselguhr. Isopropenylcyclobutane (22.4 ml) was passed over the catalyst at 200°. The resulting product has a b.p. of 96-102°; n_D^{20} 1.4406; d_4^{20} 0.7891. When the catalyzate was again passed over kieselguhr, the physical constants did not change. The hydrogenated product had a b.p. of 92-97.5° (760 mm), n_D^{20} 1.4155; d_4^{20} 0.7592. Judging from the Raman spectrum, the catalyzate was a mixture of 1,2-dimethylcyclopentanes (with a predominance of the trans form) containing traces of 1,1-dimethylcyclopentane. Isopropylidenecyclobutane (5.0 g) was passed over kieselguhr at 200°. The resulting isomerizate had constants which were close to those of the catalyzate obtained with isopropenylcyclobutane: b.p. 96-102° (760 mm); n_D^{20} 1.4400; d_4^{20} 0.7888.

Isomerization of isopropylidenecyclobutane over silica gel under conditions of adsorption chromatographic analysis. Isopropylidenecyclobutane (8.0 g) was filtered through a column containing 130 g of Grades KSM and ShSM, (a) 14, silica gel. The resulting product distilled at 100.0-104.0° and had n_D^{20} 1.4428. The hydrogenated isomerizate (5 g) had a b.p. of 92.0-97.5° (760 mm), n_D^{20} 1.4157; d_4^{20} 0.7580. Investigation of the Raman spectrum of the reaction product showed that it was a mixture of about 20% cis-1,2-dimethylcyclopentane, about 70% trans-1,2-dimethylcyclopentane, and about 10% of 1,1-dimethylcyclopentane. This same mixture was obtained previously in the work with isopropenylcyclobutane [9].

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DIALKYLTHIOBORINIC ACIDS AND CYANODIALKYLBORINES

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(Presented by Academician B. A. Kazanskii, April 3, 1959)

Esters of dialkylthioborinic acids, which may be prepared by the action of sulfur [1] or n-butylmercaptan [2] on trialkylborines, are highly reactive, considerably exceeding in reactivity their oxygen analogs. A further study of the properties of these thioesters has shown that they are capable of reacting not only with amines, but also with hydrogen sulfide and with hydrocyanic acid.

When hydrogen sulfide is passed into thio esters heated to 140-180°, dialkylthioborinic acids (I) and a mercaptan are obtained; the mercaptan distills as it is formed.

$$R_2BSC_4H_9\text{-}n + H_2S \rightarrow \left[\begin{matrix} R_2B - S - C_4H_9\text{-}n \\ | \\ SH_2 \end{matrix}\right] \rightarrow \underset{\text{(I)}}{R_2BSH} + n\text{-}C_4H_9SH$$

$$R = n\text{-}C_3H_7,\ n\text{-}C_4H_9,\ i\text{-}C_5H_{11}.$$

We used this method to prepare from n-butyl esters of dialkylthioborinic acids, di-n-propyl-, di-n-butyl-, and diisoamylthioborinic acids, which are the first representatives of this type of organoboron compound. The thio acids distill under vacuum without decomposition. On prolonged heating at 180-250°, di-n-butylthioborinic acid decomposes with the formation of hydrogen sulfide, hydrogen, butene, butane, and sulfur-containing organoboron compounds which have not yet been investigated.

n-Butyl esters of dialkylthioborinic acids react with hydrocyanic acid in the cold or on mild heating with the formation of cyanodialkylborines (III), which are the nitriles of the unknown dialkylborocarboxylic acids. When ether solutions of the n-butyl ester of di-n-butylthioborinic acid and HCN are mixed, heat is liberated, and there is first formed a colorless, gelatinous precipitate, indicating the formation in the first stage of the reaction of complex compound (II), and this rapidly undergoes further conversions:

$$R_2BSC_4H_9\text{-}n + HCN \rightarrow \underset{\text{(II)}}{[R_2BSC_4H_9\text{-}n\cdot HCN]} \rightarrow \underset{\text{(III)}}{R_2BCN} + n\text{-}C_4H_9SH$$

$$R = n\text{-}C_4H_9,\ i\text{-}C_4H_9,\ i\text{-}C_5H_{11}.$$

Cryoscopic determination of the molecular weights of these cyanodialkylborines in benzene solution showed that they are associated to some extent.

Cyanodi-n-butylborine is a substance which is stable in air, which crystallizes from ether as hexahedral plates with an m.p. of 57-58°, and which has a molecular weight four times that expected of the monomer (hence, $[(n\text{-}C_4H_9)_2BCN]_4$). Cyanodiisobutylborine is comparatively stable in air and has a sharp melting point and a molecular weight of 1900 (calculated, 151). Cyanodiisoamylborine was obtained as a thick oil which did not crystallize on standing; it exists as the dimer in benzene solution.

The infrared spectrum had an intense band with a frequency of 2256 cm^{-1}, which has been assigned to the nitrile group [3].

Cyanodialkylborines react with alcohols on heating, the reaction yielding esters of dialkylthioborinic acids and hydrocyanic acid:

$$R_2BCN + R'OH \rightarrow R_2BOR' + HCN.$$

Crystalline complex compounds (IV), which are unstable in air, are obtained by the action of amines on cyanodialkylborines:

$$R_2BCN + R'NH_2 \rightarrow R_2BCN \cdot NH_2R' \quad \text{(IV)}$$

R = n-C_4H_9, i-C_4H_9, i-C_5H_{11}

R' = n-C_4H_9, C_6H_5.

The amine complex, the infrared spectra of which were obtained with samples formed by pressing the complex with potassium bromide, have an absorption band at about 2175 cm^{-1}.

These cyanodialkylborines and their complexes with amines are the first representatives of complex organic compounds of trivalent boron containing a cyano group.

Of the cyano derivatives of negatively tetravalent boron, sodium triphenylcyanoborate, obtained by Wittig and Raff [4] by fusion of triphenylborine with sodium cyanide, and lithium cyanoborohydride, which may be synthesized by the action of hydrocyanic acid on lithium borohydride, are known.

EXPERIMENTAL PART

All operations were carried out in an atmosphere of nitrogen.

Di-n-propylthioborinic acid. In a Claisen flask fitted with a condenser arranged for distillation was placed 27 g (0.145 mole) of the n-butyl ester of di-n-propylthioboric acid [2], the liquid was heated (bath temperature 135-140°), and hydrogen sulfide was passed through the reaction mixture for 5 hours, n-butyl mercaptan distilling during this time. Fractionation of the reaction products in an atmosphere of H_2S gave 13 g (51.6%) of di-n-propylthioborinic acid b.p. 51-52°/25 mm, d_4^{19} 0.8093; n_D^{19} 1.4423.

Found%: C 55.50; 55.76; H 11.69; 11.49; B 8.44; 8.48. $C_6H_{15}BS$. Calculated%: C 55.40; H 11.62; B 8.32.

Di-n-butylthioborinic acid. Hydrogen sulfide was passed into the n-butyl ester of di-n-butylthioborinic acid [1] (5.8 g, 0.027 mole) for 2 hours at a bath temoerature of 150° and then for 3 hours at 170-180°. The reaction mixture was fractionated in an atmosphere of H_2S. There was obtained 2.1 g (49.6% of theoretical) of di-n-butylthioborinic acid, b.p. 82-83° at 21 mm; d_4^{19} 0.8175; n_D^{19} 1.4463.

Found%: C 60.80; 60.72; H 12.05; 12.00; B 6.93; 7.04; M 162.158. $C_8H_{19}BS$. Calculated%: C 60.76; H 12.11; B 6.84; M 158.1.

Diisoamylthioborinic acid. Crude n-butyl ester of diisoamylthioborinic acid prepared by the action of 11.2 g of n-butyl mercaptan on 27 g of triisoamylborine [2], was heated on a bath (bath temperature 170-180°), and hydrogen sulfide was passed into the liquid for 5 hours, the resulting n-butyl mercaptan distilling during the course of the reaction. There was obtained 19.1 g (84.7%) of diisoamylthioborinic acid with a b.p. of 80-81° at 3 mm; d_4^{20} 0.8179; n_D^{20} 1.4506.

Found%: C 64.94; 65.10; H 12.38; 12.68; B 5.94; 6.02. $C_{10}H_{23}BS$. Calculated%: C 64.51; H 12.45; B 5.81.

The dialkylthioborinic acids were colorless liquids with a disagreeable odor; they were soluble in organic solvents, and were readily oxidized and hydrolyzed.

Cyanodi-n-butylborine. 4 ml of hydrocyanic acid in 5 ml of ether was added to a solution of 14.9 ml (0.07 mole) of the n-butyl ester of di-n-butylthioborinic acid [1] in 10 ml of absolute ether. Heat was evolved, and a white gelatinous precipitate formed; the precipitate rapidly disappeared, and the reaction mixture first stratified and then crystallized on standing. The precipitate was washed twice with ether (7-ml portions), and dried under vacuum. There was obtained 10.08 g (95.8%) of cyanodi-n-butylborine, m.p. 62.5-63.5° (in a sealed capillary). The substance crystallized from ether in the form of hexahedral plates, m.p. 57-58° (in a sealed capillary).

Found%: C 71.68; 71.44; H 12.33; 12.17; B 7.06; 7.41; M 541. $C_9H_{18}BN$. Calculated%: C 71.55; H 12.01; B 7.16; M 151.

Cyanodi-n-butylborine was a colorless substance with a slight odor of hydrocyanic acid; it was soluble in benzene, acetone, carbon tetrachloride, and chloroform, and was insoluble in cold alcohol. It was stable toward atmospheric oxygen (there was almost no change in its melting point after it had stood in an open box for a month).

The action of n-butyl alcohol on cyanodi-n-butylborine. A mixture of 3.3 g (0.022 mole) of cyanodi-n-butylborine and 3 ml (0.033 mole) of n-butyl alcohol was heated for 0.5 hour at 120° (until boiling of the mixture ceased), hydrocyanic acid distilling during the course of the heating. 0.58 g (98.3% of theoretical) of HCN was envolved. The residue was fractionated under vacuum. 3.07 g (77.5% of theoretical) of the n-butyl ester of di-n-butylborinic acid was obtained; b.p. 106.5-107°/15 mm, n_D^{20} 1.4230 (literature value: b.p. 120-121°/24 mm [5]).

Cyanodiisobutylborine. 5 ml of hydrocyanic acid in 10 ml of ether was added to a solution of 12.8 ml (0.057 mole) of the n-butyl ester of diisobutylthioborinic acid [2] in 100 ml of ether. After the removal under vacuum of the ether and the n-butyl mercaptan resulting from the reaction, there remained a thick, colorless, glassy substance, which hardened on standing for a month. The compound was a polymer of cyanodiisobutylborine; it softened at 65°, and melted completely at 145° (in a sealed capillary).

Found%: C 71.73; 71.49; H 12.03; 11.94; B 7.08; 6.81; M 1902. $C_9H_{18}BN$. Calculated%: C 71.55; H 12.01; B 7.11; M 151.

The cyanodiisobutylborine polymer was stable in air, had a slight odor of hydrocyanic acid, and was difficultly soluble in benzene and ether (at room temperature).

Cyanodiisoamylborine. A solution of 12.1 g (0.05 mole) of the n-butyl ester of diisoamylthioborinic acid [2] and 6 ml of hydrocyanic acid in 35 ml of absolute ether was heated at the boiling point for 15 minutes. After evaporation under vacuum of the excess hydrocyanic acid, the ether, and the n-butyl mercaptan formed in the reaction, 8.9 g (99.5%) of crude cyanodiisoamylborine was obtained; the material did not crystallize, either from solvents or on standing for a month. The crude reaction product was analyzed.

Found%: C 71.08; 71.06; H 12.58; 12.50; B 6.29; 6.51; M 358, 360. $C_{11}H_{22}BN$. Calculated%: C 73.76; H 12.38; B 6.04; M 179.2.

The cyanodiisoamylborine was a thick oil which had a slight odor of hydrocyanic acid; it was soluble in organic solvents.

Complex of cyanodiisobutylborine with aniline. A mixture of 6.43 g (0.043 mole) of cyanodiisobutylborine and 6.5 ml (0.07 mole) of aniline in 30 ml of absolute ether was heated to boiling. The resulting precipitate was washed with ether. 7.05 g (67.8%) of a complex of cyanodiisobutylborine with aniline was obtained; m.p. 101-102° (in a sealed capillary). After recrystallization from ether, the substance had an m.p. of 96-97° (in a sealed capillary).

Found%: C 73.43; 73.42; H 10.51; 10.33; B 4.62; 4.65; M 252, 249. $C_{15}H_{25}BN_2$. Calculated%: C 73.77; H 10.32; B 4.43; M 244.

Complex of cyanodiisobutylborine with n-butylamine. A solution of 2.07g (0.014 mole) of cyanodiisobutylborine and 1.9 ml of n-butylamine in 30 ml of absolute ether was heated at the boiling point for 30 minutes; the solvent was then evaporated under vacuum until half of the original volume remained, and the resulting precipitate was filtered and washed with ether. 2.88 g (93.8%) of the n-butylamine complex with cyanodiisobutylborine was obtained in the form of colorless needles with an m.p. of 117-117.5° (in a sealed capillary).

Found%: C 69.53; 69.73; H 12.87; 13.03; B 4.83; 4.75. $C_{13}H_{32}BN_3$. Calculated%: C 69.64; H 13.04; B 4.83.

Complex of cyanodiisoamylborine with aniline. In a manner analogous to that described above, from 8.64 g (0.048 mole) of cyanodiisoamylborine and 4.9 ml (0.054 mole) of aniline in 15 ml of absolute ether was obtained 6.44 g (50.4%) of the complex of cyanodiisoamylborine with aniline; m.p. 110-112°. Two recrystallizations from ether gave 2.25 g of the complex with an m.p. of 115-115.5° (in sealed capillary).

Found%: C 74.98; 74.96; H 10.83; 10.75; B 4.08; 4.12; M 278, 286. $C_{17}H_{29}BN_2$. Calculated%: C 75.00; H 10.74; B 3.97; M 272.2

Complex of cyanodi-n-butylborine with aniline. 1.9 ml (0.021 mole) of aniline in 2 ml of absolute ether was added to a solution of 2.58 g (0.017 mole) of cyanodi-n-butylborine in 15 ml of absolute ether. The resulting white precipitate was washed twice with ether (3-4-ml portions) and dried under vacuum. 2.35 g (61% of theoretical) of the complex of cyanodi-n-butylborine with aniline was obtained; m.p. 110-111.5°. After two recrystallizations from absolute ether, the substance had an m.p. of 111-112° (in a sealed capillary).

Found %: C 73.90; 73.52; H 10.34; 10.37; B 4.32; 4.80; M 213. $C_{15}H_{25}BN_2$. Calculated %: C 73.77; H 10.32; B 4.43; M 244.

All of the amine complexes of cyanodialkylborines are colorless crystalline substances, soluble in acetone, sparingly soluble in benzene and ether, and insoluble in carbon tetrachloride. The aniline complexes oxidize readily in air, and their benzene solutions darken on standing.

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THE INTERACTION OF 1,1,1-TRICHLOROPROPENE WITH MERCAPTANS

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At least three types of reactions of 1,1,1-trichloropropene are known [1]: electrophilic addition, for example, of hypobromous acid, which proceeds contrary to Markownikoff's rule; nucleophilic addition, which proceeds with allylic rearrangement; and radical addition, which proceeds with rearrangement of intermediate radicals of type "A" to radicals of type "B":

$$\underset{\text{A}}{CCl_3-\dot{C}H-CH_2X} \rightarrow \underset{\text{B}}{\dot{C}Cl_2-CHCl-CH_2X}$$

In the present work, the addition of thiophenol and benzyl mercaptan to 3,3,3-trichloropropene was investigated. When the reaction of 1,1,1-trichloropropene with thiophenol was carried out under the action of incandescent lamp (100 watts), 2,3,3-trichloropropyl phenyl sulfide was obtained according to the scheme:

$$CCl_3-CH=CH_2 + C_6H_5SH \rightarrow CCl_2=CH-CH_2SC_6H_5$$

The structure of this sulfide was proved by alternate synthesis from 1,1,2,3,3-pentachloropropene and sodium thiophenolate. In addition, the presence of halogen atoms on neighboring carbon atoms was proved by partial dechlorination of sulfide (I) with the formation of a mixture of the cis and trans isomers of 3-chloropropen-2-yl phenyl sulfide [3-chloroallyl phenyl sulfide]; the trans isomer was isolated and identified with a sample of 3-chloropropen-2-yl phenyl sulfide prepared by a known method [2]. Thus, under these conditions, the reaction proceeds by a homolytic mechanism. When the reaction with benzyl mercaptan was carried out under analogous conditions, two products were formed— 2,3,3-trichloropropyl benzyl sulfide (II) and 3,3-dichloropropen-2-yl benzyl sulfide (III) [3,3-dichloroallyl benzyl sulfide]— with a predominance of the latter.

The structures of sulfides (II) and (III) were proved by alternate synthesis from the corresponding alkyl halides and sodium benzyl mercaptide.

Moreover, it was established that hydrogen chloride was evolved during the reaction in an amount corresponding to the amount of sulfide (III) obtained. The formation of these products can be explained by the following schemes:

$$CCl_3-CH=CH_2 + \dot{S}CH_2C_6H_5 \rightarrow \underset{\text{(IV)}}{CCl_3-\dot{C}H-CH_2SCH_2C_6H_5}$$

$$\text{IV} \xrightarrow{\text{isomerization}} \underset{\text{(V)}}{\dot{C}Cl_2-CHClCH_2SCH_2C_6H_5}$$

$$\text{V} + HSCH_2C_6H_5 \rightarrow \begin{cases} \underset{\text{(II)}}{HCCl_2-CHClCH_2SCH_2C_6H_5} + \dot{S}CH_2C_6H_5 \\ \underset{\text{(III)}}{CCl_2=CH-CH_2SCH_2C_6H_5} + HCl + \dot{S}CH_2C_6H_5 \end{cases}$$

It is less probable that sulfide (III) was formed by nucleophilic addition.

When the reaction of 1,1,1-trichloropropene with thiophenol was carried out in the presence of sulfur as an inhibitor of radical processes, 3,3,3-trichloropropyl phenyl sulfide was obtained; the structure of this compound was proved by a study of the i.r. spectrum, which had no frequencies characteristic of a methyl group.

EXPERIMENTAL PART

1. Interaction of 1,1,1-trichloropropene with thiophenol. a) A mixture of 29 g (0.2 mole) 1,1,1-trichloropropene and 11 g (0.1 mole) of thiophenol was agitated for 4 hours under irradiation from an incandescent lamp (100 watts, temperature inside the flask 80-90°). After distillation of the starting materials, fractionation gave 8.7 g (34.5% of theoretical) of 2,3,3-trichloropropyl phenyl sulfide, which, after a second distillation, had an m.p. of 119° at 2 mm; n_{β}^{20} 1.5903; d_4^{20} 1.3515.

Found %: C 43.29; 43.41; H 3.45; 3.37. $C_9H_9Cl_3S$. Calculated %: C 42.27; H 3.52.

4.5 g of the sulfide was oxidized by heating with hydrogen peroxide in glacial acetic acid. There was obtained 4 g (80% of theoretical) of 2,3,3-trichloropropyl phenyl sulfone, m.p. 61°-62° (from alcohol).

Found %: C 37.44; 37.57; H 3.14; 3.14; Cl 37.15; 37.01; S 11.08; 11.29. $C_9H_9Cl_3SO_2$. Calculated %: C 37.56; H 3.13; Cl 37.04; S 11.13.

A mixture of this sulfone with 2,3,3-trichloropropyl phenyl sulfone prepared by a known method (Experiment 4) showed no depression of the melting point.

b) A mixture of 43 g (0.3 mole) of 1,1,1-trichloropropene, 29 g (0.27 mole) of thiophenol, and 2 g of elemental sulfur was heated at 115° for 5 hours. Distillation of the starting materials followed by distillation of the product gave 19 g (35.4% of theoretical) of 3,3,3-trichloropropyl phenyl sulfide, which, after a second distillation, had a b.p. of 119° at 2 mm; n_D^{20} 1.5838; d_4^{20} 1.3650.

Found %: C 42.88; 42.76; H 3.55; 3.51. $C_9H_9Cl_3S$. Calculated %: C 42.27; H 3.52.

Oxidation of the sulfide gave 3,3,3-trichloropropyl phenyl sulfone, m.p. 104-105° (from alcohol).

Found %: C 37.54; 37.73; H 3.21; 3.17; Cl 36.62; 36.65; S 11.15; 11.02. $C_9H_9Cl_3SO_2$. Calculated %: C 37.56; H 3.13; Cl 37.04; S 11.13.

2. Interaction of 2,3,3-trichloropropyl phenyl sulfide with zinc. A solution of 9.7 g of 2,3,3-trichloropropyl phenyl sulfide in methanol was heated with 3 g of zinc dust for 14 hours. After dilution with water, the reaction mixture was extracted with ether. The ether was distilled, and the residue was distilled under vacuum. There was obtained 3.5 g of 3-chloropropen-2-yl phenyl sulfide with a b.p. 79-80° at 1 mm, n_{β}^{20} 1.5910; d_4^{20} 1.1783. MR found, 52.87. MR calculated, 52.63.

Found %: C 58.29; 58.37; H 5.00; 4.92; Cl 19.30; 19.17. C_9H_9ClS. Calculated %: C 58.53; H 4.87; Cl 19.24.

Oxidation of 3.3 g of the sulfide gave 2.5 g of an oily mixture of sulfides, from which we were able to isolate 1.3 g of crystalline trans-3-chloropropen-2-yl phenyl sulfone with an m.p. of 67° (from alcohol). A mixture with trans-3-chloroprepen-2-yl phenyl sulfone prepared by a known method (Experiment 4) showed no depression of the melting point.

3. Interaction of 1,1,1-trichloropropene with benzyl mercaptan. A mixture of 43.4 g (0.3 mole) of 1,1,1-trichloropropene and 24.8 g (0.2 mole) of benzylmercaptan was irradiated with an incandescent lamp (100 watts) for 9 hours at a temperature of 110-115°. After distillation of the starting materials, the residue was fractionated, and the following fractions were collected:

1. B.p. 98-103° at 1 mm; 18.2 g.
2. B.p. 120-130° at 1 mm; 5.8 g.

A second distillation of the first fraction gave 3,3-dichloropropen-2-yl benzyl sulfide, b.p. 90.5-91° at 0.5 mm, n_D^{20} 1.5845; d_4^{20} 1.2551. MR found, 62.17; MR calculated, 62.12.

Found %: C 50.86; 50.73; H 4.20; 4.23. $C_{10}H_{10}Cl_2S$. Calculated %: C 51.50; H 4.29.

Oxidation of 1.2 g of this sulfide gave 1.2 g (88% of theoretical) of the sulfone, m.p. 93-94° (from alcohol). A mixture with 3,3-dichoropropen-2-yl benzyl prepared by a known method (Experiment 4) showed no depression of the melting point.

A second distillation of the second fraction gave 2,3,3-trichloropropyl benzyl sulfide with a b.p. of 114-115° at 0.5 mm, n_D^{20} 1.5793, d_4^{20} 1.3244. MR found, 67.65; MR calculated, 67.45.

Found %: C 44.74; 44.66; H 4.12; 4.14; Cl 39.16; 38.94 $C_{10}H_{11}Cl_3S$. Calculated %: C 44.52; H 4.08; Cl 39.52.

Oxidation of 1.5 g of the sulfide gave 1.5 g (89% of theoretical) of the sulfone with an m.p. of 100-101° (from alcohol).

Found %: C 39.77; 39.63; H 3.61; 3.62; Cl 35.54; 35.30 $C_{10}H_{11}Cl_3SO_2$. Calculated %: C 39.80; H 3.64; Cl 35.32.

A mixture with 2,3,3-trichloropropyl benzyl sulfone prepared by a known method (Experiment 4) showed no depression of the melting point.

In a special experiment in which 0.15 mole of benzyl mercaptan was used, 0.035 mole of hydrogen chloride was obtained, which corresponds approximately with the amount of 3,3-dichloropropen-2-yl benzyl sulfide (10.5 g).

4. Interaction of sodium phenyl and benzyl mercaptides with $CCl_2 = CH - CH_2Cl$, $CHCl = CH - CH_2Cl$, $CHCl_2 - CHCl - CH_2Br$. a) At a reaction temperature of 50-60°, from 19 g (0.084 mole) of 1-bromo-2,3,3-trichloropropane and sodium thiophenolate (from 10 g of thiophenol and 1.93 g of sodium) in a medium of glacial acetic acid was obtained 11.9 g (55.6% of theoretical) of 2,3,3-trichloropropyl phenyl sulfide with a b.p. of 131° at 3 mm, n_D^{20} 1.5885, d_4^{20} 1.3574. Oxidation of 3 g of the sulfide gave 2.7 g (79.5% of theoretical) of 2,3,3-trichloropropyl phenyl sulfone, m.p. 61-62° (from alcohol).

Similarly were prepared:

b) From trans-1,3-dichloropropene and C_6H_5SNa — trans-3-chloropropen-2-yl phenyl sulfide (46.2% of theoretical), b.p. 69° at 0.5 mm, n_D^{20} 1.5922, d_4^{20} 1.1706. M.p. of sulfone, 68.5° (from alcohol).

Found %: C 50.03; 50.10; H 4.11; 4.18; Cl 16.07; 16.28 $C_9H_9ClO_2S$. Calculated %: C 49.88; H 4.15; Cl 16.40.

c) From 1-bromo-2,2,3-trichloropropane and $C_6H_5CH_2SNa$ — 2,3,3-trichloropropyl benzyl sulfide, b.p. 123-124° at 1 mm; m.p. of sulfone, 100° (from alcohol).

d) From 1,1,3-trichloro-1-propene and $C_6H_5CH_2SNa$ — 3,3-dichloropropen-2-yl benzyl sulfide, b.p. 98-99° at 1 mm, n_D^{20} 1.5845, d_4^{20} 1.2580.

Found %: C 51.98; 51.88; H 4.09; 4.17 $C_{12}H_{12}Cl_2S$. Calculated %: C 51.50; H 4.29.

M.p. of sulfone, 93.5-94.5° (from alcohol).

Found %: C 45.17; 45.18; H 3.52; 3.62; Cl 26.41; 26.62 $C_{10}H_{10}Cl_2SO_2$. Calculated %: C 45.28; H 3.77; Cl 26.80.

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THE EXTRACTION OF NITRIC ACID WITH DERIVATIVES OF BUTYLPHOSPHINIC ACIDS

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The present communication reports a part of the work in which the properties of a number of butylphosphorus compounds as extractants have been studied; these compounds include tributyl phosphate (TBP) $(C_4H_9O)_3PO$; the dibutyl ester of butylphosphonic acid (DBBP) $(C_4H_9O)_2C_4H_9PO$; the butyl ester of dibutylphosphinic acid (BEDP) $(C_4H_9O)(C_4H_9)_2PO$; and tributylphosphine oxide (TBPO) $(C_4H_9)_3PO$.

The work of L.L. Berger [1] showed that derivatives of butylphosphinic acids are more effective than TBP as extractants for such important elements as uranium and plutonium.

In view of the fact that the extraction of uranium and plutonium is usually carried out in nitric acid solutions of these elements, it is necessary to study the distribution of nitric acid between aqueous solutions and the indicated organic solvents. The literature contains data on the behavior of nitric acid during extractions with TBP (the first member of the series studied [2-4]). Information on the extraction of nitric acid by other representatives of this series was not found. The latter circumstance served as an incentive to investigate the extraction of nitric acid by esters of butylphosphinic acids and by TBPO.

The dependence of the distribution of nitric acid on the concentration of the extractant and on the presence of uranyl nitrate in the solution was studied in the present work. The experiments were carried out in separatory funnels at a volume ratio of aqueous to organic phase of 1:1. Saturated high-boiling hydrocarbons (SHH) and carbon tetrachloride were used as diluents for the extractants. All of the extractants used were subjected to a preliminary purification. The concentration of nitric acid in the equilibrium phases was determined by direct titration with 0.1 N alkali, and in the presence of uranyl nitrate, it was determined by potentiometric titration. Titration of the organic phase was carried out in aqueous alcohol solution. The indicator was Methyl red. The initial concentration of nitric acid was constant and equal to 1 N in all experiments. The concentration of uranyl nitrate in the aqueous solution was 30 g/liter.

According to the data of Table 1, which presents the results of the experiments, the extraction of nitric acid increased significantly with an increase in the concentration of the extractants in SHH.

On going through the series from TBP to TBPO, the extraction of nitric acid increased sharply (see Figure 1). Thus, for example, a comparison of the extraction of nitric acid by 10% solutions of TBP and BEDP in SHH and of 10% TBPO in CCl_4 shows that TBP extracted 3%, BEDP 19%, and TBPO 30% of the acid.

During the extraction of nitric acid with BEDP, an anomalous decrease in the extraction of acid as compared to extraction with other extractants of this series was noted when the concentration of BEDP in the diluent was increased above ~50% (see Figure 1 and Table 1).

A second organic phase separated during the extraction of nitric acid with a 5% solution of TBPO in SHH*;

* Solubility limit of TBPO in SHH is ~5%.

TABLE 1

Extractant	Conc. of Extractant in diluent, vol. %	Normality of HNO_3 in organic phase	Normality of HNO_3 in aqueous phase*	Per cent extraction
TBP	5	0,03	0,97	3
	20	0,084	0,92	8,4
	100	0,653	0,347	65,3
DEBP	5	0,06	0,94	6
	10	0,101	0,899	10,1
	20	0,2	0,802	19,8
	100	0,86	0,14	86,0
BEDP	5	0,1	0,9	10
	10	0,186	0,814	18,6
	20	0,316	0,684	31,5
	50	0,52	0,48	52,0
	100	0,73	0,27	73,0
TBPO in CCl_4	5	0,15	0,85	14
	10	0,288	0,712	28,8
TBPO in SHH	5	0,026	0,894	2,6
SHH	100	0,001	0,999	0,1

* The normality of HNO_3 in the aqueous phase was calculated as the difference between the initial HNO_3 concentration and the concentration in the organic phase.

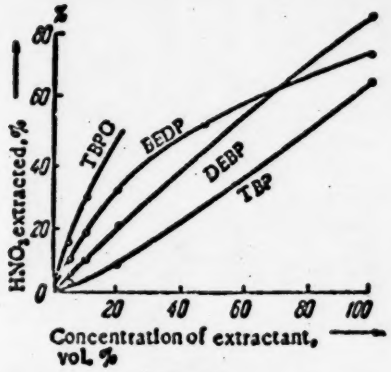

Fig. 1

by analogy to the compound previously established for TBP, this phase was apparently a compound of TBPO with HNO_3. Confirmation of this is the fact that in the second organic phase, which comprised 1/20 of the original volume of extractant solution, the molar concentration of nitric acid was 2.5 times that in the original aqueous solution. Therefore, extraction of HNO_3 into the first organic phase was 2.6%, and extraction into the second phase was 8%. Moreover, when a fresh portion of undiluted TBPO was added to the total organic portion, there was an increase in the volume of the second organic phase owing to combination of TBPO with nitric acid. After the second organic phase had been dried for 5 hours in a vacuum desiccator, its density was 0.978 g/cc. Formation of a second organic phase was not detected when CCl_4 was used as the diluent, apparently owing to the higher solubility of the HNO_3 solvate in CCl_4 as compared to that in SHH*. In the case of CCl_4, extraction of nitric acid into the organic phase was 15% for 5% TBPO and 28% for 10% TBPO.

Table 2 presents the results of experiments on the extraction of nitric acid by the solvents investigated with uranyl nitrate present in the aqueous solution (30 g/liter). With extractant concentrations of from 0 to ~50%, there was a regular decrease in extraction of acid in the series from TBP to TBPO, which was probably due to the increase in the extraction of uranyl nitrate and, consequently, to displacement of the nitric acid from the organic phase into the aqueous phase. This effect was greater the more effective the extractant for the extraction of uranyl nitrate [1]. It may be seen from the data of Table 2 that extraction of nitric acid by BEDP at concentrations in SHH of above ~50% was anomalous as compared to the other extractants, both in the presence and in the absence of uranyl nitrate (see Table 1).

Consequently, in contrast to the effect with other extractants, beginning with ~50% BEDP the effect of the presence of uranyl nitrate on the extraction of nitric acid decreased and became so insignificant that it had almost no effect on the amount of acid extracted.

* Solubility limit of TBPO in CCl_4 is ~10%.

TABLE 2

Extractant	Conc. of extractant in diluent, vol.% (SHH)	Normality of HNO_3 in organic phase	Normality of HNO_3 in aqueous phase	Per cent extraction
TBP	100	0,59	0,38	60,8
DEBP	5	0,06	0,91	6,1
	20	0,13	0,84	13,4
	100	0,52	0,45	53
BEDP	5	0,03	0,94	3,1
	20	0,08	0,89	8,2
	50*	0,52	0,48	52
	100*	0,81	0,19	73,6
TBPO	5	0,02	0,95	2,08

* Initial concentration in the aqueous phase was 1 N with respect to HNO_3; in all remaining experiments, it was 0.97 N.

All of our data indicate that the extraction of nitric acid by the extractants studied increases in the series TBP < DEBP < BEDP < TBPO; moreover, it is possible to separate a compound of the acid with TBPO.

The anomalous behavior of BEDP with respect to HNO_3, both in the presence and in the absence of uranyl nitrate, is still unexplained.

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CERTAIN CHEMICAL PROPERTIES OF PHENYLTITANIUM TRIISOPROPYLATE AND ITS CATALYTIC ACTIVITY DURING THE POLYMERIZATION OF OLEFINS

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In the investigation of the mechanism of the polymerization of olefins with Ziegler catalysts, the work of Natta and co-workers [1,2] on the catalytic activity of dicyclopentadienyldiphenyltitanium for ethylene polymerization is of great interest. These authors showed that this compound by itself does not cause polymerization of ethylene, but with the addition of a trialkylaluminum or titanium tetrachloride a catalyst is obtained which polymerizes ethylene with the formation of solid polymer. But $(C_6H_5)_2Ti(C_5H_5)_2$ differs basically in structure from the usual organometallic compounds with covalent Me—C bonds.

A method for the synthesis of a purely covalent organotitanium compound—phenyltitanium isopropylate—has been described in the literature [3,4]. This compound is an initiator of the polymerization of styrene to solid polymer, which the authors explain by the ease with which it decomposes with the formation of phenyl radicals. However, chemical reactions peculiar to organometallic compounds have received little study in the case of phenyltitanium triisopropylate. Therefore, we considered it of interest to investigate certain chemical properties of this compound and its catalytic activity in the polymerization of unsaturated compounds, both by itself and with the addition of AlR_3 or $TiCl_4$, i.e., with the same promoters which have been used with $(C_6H_5)_2Ti(C_5H_5)_2$. When $C_6H_5Ti(i\text{-}OC_3H_7)_3$ (1.16 g), which was prepared by a method described in the literature, was reacted with $HgCl_2$ (1.20 g) in benzene solution at a temperature of 65-68° and a reaction time of 5 hours, phenylmercury chloride was obtained (yield, 0.5 g; m.p. 249-250°; literature m.p. 250.5°) evidently as a consequence of a heterolytic exchange between the reactants, a reaction which is characteristic of organometallic compounds. It is known [5] that certain true organometallic compounds form organomercury compounds when acted upon by metallic mercury. No organic mercury compound was obtained when a solution of phenyltitanium triisopropylate in benzene was heated with mercury for 20 hours at a temperature of 90-100°. A more detailed investigation of this reaction was not carried out.

The phenyltitanium triisopropylate synthesized by us did initiate polymerization of styrene, but only traces of liquid polymer were found in the case of propylene. A number of other monomers - vinyl chloride, methyl methacrylate, butyl methacrylate, acrylonitrile - did not polymerize in the presence of phenyltitanium triisopropylate. It was established that the system $Al(C_2H_5)_3 - C_6H_5Ti(i\text{-}OC_3H_7)_3$ causes polymerization of propylene at a temperature of 90-100° with the formation of liquid polymer, but the yield of polymer did not exceed 30-35%. With the addition of titanium tetrachloride to phenyltitanium triisopropylate, a catalyst was obtained which brought about more intense polymerization of propylene at a temperature of 90-100° with the formation of liquid polymer having a molecular weight of 144-545. The yield of polymer depends to a considerable extent on the molar ratio of the catalyst components (Figure 1). As may be seen from Figure 1, at a molar ratio of $TiCl_4$ to $C_6H_5Ti(i\text{-}OC_3H_7)_3$ in the range of 1 to 1.5 the yield of polymer was low, while at a ratio of from 2 to 4 propylene conversion was 96-98%.

In Figure 2 is shown the effect of the amount of catalyst on polymer yield. The propylene used in the polymerization studies was obtained by dehydration of isopropyl alcohol, and was carefully purified. All of the other monomers ("chemically pure" grade) were distilled before use. Polymerization was carried out in molybdenum glass ampoules having a volume of about 10 ml. The catalyst and monomer were charged to the ampoules in

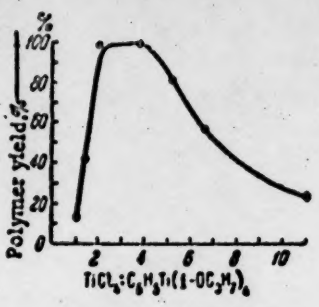

Fig. 1. The effect of the mole ratio of $TiCl_4$ to $C_6H_5Ti(i\text{-}OC_3H_7)_3$ on polymer yield at t=90-100° and a reaction time of 5 hours.

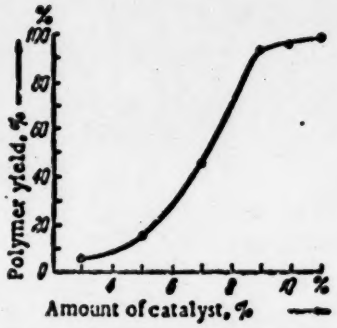

Fig. 2. Dependence of polymer yield on amount of catalyst at t = 90-100° and a reaction time of 5 hours. Molar ratio of $TiCl_4$ to $C_6H_5Ti(i\text{-}OC_3H_7)_3$ = 2.5.

an atmosphere of nitrogen. The charged ampoules were placed in an electric furnace installed on a shaker, and there they were heated for 4-5 hours.

In order to determine the mechanism of the action of the catalytic system $C_6H_5Ti(i\text{-}OC_3H_7)_3$—$TiCl_4$ during polymerization, the interaction of these compounds was investigated at a molar ratio of $TiCl_4$ to $C_6H_5Ti(i\text{-}OC_3H_7)_3$ of about 2.5 in an organic solvent (hexane and benzene) at room temperature. To a solution of phenyltitanium triisopropylate (3.76 g) in dry hexane (50 ml) was added, with continuous stirring and over a period of 40 minutes, a solution of $TiCl_4$ (6.0 g) in hexane (20 ml), after which the reaction mixture was stirred for an additional 2 hours. The following compounds were isolated from the reaction mixture and identified: biphenyl (0.90 g, 93.5 % yield calculated on the content of phenyl groups in the starting material), m.p. 69-70° (recrystallized from petroleum ether), literature m.p. 70.5°. A mixture with a sample of pure biphenyl melted without depression of the melting point. There was also a titanium compound corresponding in composition to triisopropoxytitanium chloride.

Found %: Cl 49.30; Ti 22.55; $i\text{-}C_3H_7O$ 27.05 $i\text{-}C_3H_7OTiCl_3$.
Calculated %: Cl 49.90; Ti 22.45; $i\text{-}C_3H_7O$ 27.65.

A compound containing tetravalent titanium (1.46 g) was also found. Found, %: $Ti_{tot.}$ 26.40; Ti^{+3} 13.85; Cl 42.98; $i\text{-}C_3H_7O$ 31.70. The same compounds were found when the reaction was carried out in benzene solution.

The formation of biphenyl could be the result either of the direct interaction of monophenyl titanium derivatives or of the interaction of free phenyl radicals resulting from the decomposition of phenyltitanium triisopropylate. It is also possible that the interactions of the compounds indicated above form polyphenyl derivatives of titanium, which, as is well known [6], are extremely unstable and rapidly decompose. Decomposition of these compounds could proceed with the formation of biphenyl. In order to clarify a possible scheme for the interaction of $C_6H_5Ti(i\text{-}OC_3H_7)_3$ with $TiCl_4$, the reaction between these compounds was carried out in solution in labeled benzene with an initial activity of 1100 imp /min.* At the conclusion of the reaction, the biphenyl was separated from the reaction mixture by steam distillation. After a two-stage steam distillation, the biphenyl had practically no activity (only 5-10 imp / minute was detected). (The compounds were converted to CO_2, and the activity of the CO_2 was determined with an internal gas-flow meter by the method developed at the Chair of Radiochemistry at Lobachevskii Gorki State University). The results show that there were no free phenyl radicals present in the reaction mixture.

On the basis of the experimental data, the following scheme may be proposed for the interaction of the above compounds:

$$C_6H_5Ti(i\text{-}OC_3H_7)_3 + 2TiCl_4 \rightarrow C_6H_5Ti\begin{matrix}Cl_3\\ \diagdown\\ \diagup\\ i\text{-}OC_3H_7\end{matrix} + 2\,i\text{-}C_3H_7OTiCl_3$$

$$\downarrow$$

$$1/2\,(C_6H_5)_2 + i\text{-}C_3H_7OTiCl_3$$

When heated to a temperature of 45-50°, the compound corresponding in composition to triisopropoxytitanium chloride readily decomposed with the formation of titanium oxychloride, which is an active catalyst for the poly-

* The reaction in labeled benzene was carried out by V. A. Dodonov.

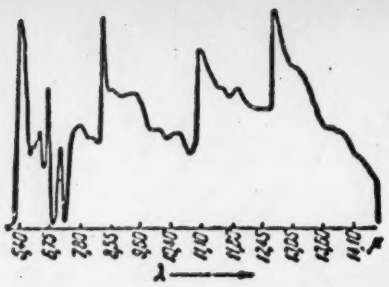

Fig. 3. I. r. spectrum of polypropylene prepared in the presence of $C_6H_5Ti(i\text{-}OC_3H_7)_3$–$TiCl_4$ catalyst.

merization of propylene to liquid polymer; this is characteristic of trichloroalkoxy derivatives of titanium with secondary and tertiary organic groups [7]. The compound containing trivalent titanium was found to be practically inactive for the polymerization of propylene.

On the basis of the present investigation, it is possible to conclude that in polymerizations with the catalyst system $TiCl_4$–$C_6H_5Ti(i\text{-}OC_3H_7)_3$, the actual catalyst is titanium oxychloride, which is formed as a result of a series of reactions preceding the polymerization process, while phenyl radicals do not take any part in the polymerization process. This conclusion is also confirmed by the absence of phenyl groups in the polymer obtained in the presence of the $C_6H_5Ti(i\text{-}OC_3H_7)_3$–$TiCl_4$ catalyst (determined by means of the i.r. spectrum of the polymer, Figure 3).

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** Original Russian pagination. See C.B. Translation.

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THE NIOBIUM ANALOG OF PHOSPHONITRILE CHLORIDE

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As is well known, for some time past interest in high polymers of inorganic origin has been sharply increasing. In this connection, certain long-known inorganic compounds known to be polymeric, which had not previously attracted the attention of investigators, have now been subjected to close study. In particular, and, perhaps especially, this relates to phosphonitrile chlorides.

It seemed to be of interest to inquire into the possible existence of derivatives of this same type of elements which are analogs of phosphorus. We were unable to find any data on such compounds in the literature.

In contrast to phosphorus, bonds with nitrogen are not very characteristic of elements of the arsenic subgroup, which may be due to their different (as compared to phosphorus) electronic configuration in their higher valence states (the presence of eighteen electrons in the outer shell). On the other hand, the elements of the vanadium subgroup are analogous to phosphorus in their higher valence states with regard to the structure of the outer electron shells, and they form stable nitrides. Of these elements, the most suitable for setting up the initial investigation is niobium, the higher chlorides of which (unlike those of vanadium) can be directly used in an experimental process which is analogous to the preparation of phosphonitrile chlorides.

There are a number of papers [1-6] in the literature relating to the preparation of phosphonitrile chlorides by the reactions:

$$n\,PCl_5 + n\,NH_4Cl = (PNCl_2)_n + 4n\,HCl.$$

From our point of view, the most satisfactory method for the preparation of a niobium analog of phosphonitrile chlorides appeared to be one which would permit observation of the progress of the reaction by means of the rate of liberation of hydrogen chloride [4].

Reaction in the initial mixture of niobium pentachloride with a large excess of ammonium chloride became appreciable (according to the liberation of HCl) even under ordinary conditions, but the reaction became complete only at higher temperatures (250-260°). Upon completion of the process, the excess unreacted NH_4Cl and $NbCl_5$ was removed by heating to 325° under reduced pressure. The resulting final product was a finely crystalline, yellowish-brown powder which was stable in air but which was slowly hydrolyzed by water. This substance was not appreciably soluble in benzene, toluene, dichloroethane, carbon sulfide, carbon tetrachloride, or ethyl ether.

A complete analysis of this compound was carried out after it had been decomposed in hydrofluoric acid (~20%). The niobium content of the samples was determined by the tannin method, chlorine was determined by precipitation with silver nitrate, and nitrogen was determined by distillation of the ammonia into standard acid. Averages of four determinations, which differed little among themselves, gave atomic ratios of Nb:N:Cl = 1:1.07:2.10, which are very close to the theoretical ratios for $NbNCl_2$. Determination of the density of the compound at 20° in toluene gave a value of 2.05 ± 0.05.

On the thermogram obtained during the decomposition of the $NbNCl_2$ in an atmosphere of argon there was observed a single endothermic effect which lay in the temperature range of 420-460° and which corresponded to thermal decomposition according to the scheme:

$$NbNCl_2 \rightarrow NbN + Cl_2.$$

That the decomposition occurred according to this reaction was confirmed by a complete analysis of the solid residue and a qualitative analysis of the gaseous reaction products.

The results of an x-ray investigation indicated that this compound was a single compound (difference between the intensity curve of $NbNCl_2$ and those of $NbCl_5$, NH_4Cl, and NbN).

A microscopic investigation of the compound showed that it is anisotropic. An attempt to determine its refractive index was unsuccessful, since it was so high that even the use of an immersion liquid with a refractive index of 1.986 was insufficient.

The data presented above show that our original assumption of the possibility of the existence of a niobium derivative analogous in composition to phosphonitrile chloride has been confirmed. The study of the properties of this substance will be continued.

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OLITORIN – A NEW CARDIAC GLYCOSIDE FROM THE LONG-POD JUTE (CORCHORUS OLITORIUS L.)

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Kharkov Scientific Research Chemical-Pharmaceutical Institute

(Presented by Academician A. I. Oparin, April 11, 1959)

The long-pod jute is a semishrub which grows wild in regions with a tropical climate. It is widely cultivated in the Soviet Union as a commercial fiber plant [1]. Information on the presence in the seeds of certain species of jute of substances having an effect on the heart began to appear in the literature toward the close of the last century and the beginning of the twentieth century [2,3]. Over ten cardiac glycosides or aglycons have been separated from the seeds; a part of these were identified as strophanthidin by Reichstein and co-workers [4], and in 1954, M. Frerejacque and M. Durgeat [5] separated from the fermented seeds of C. olitorius and C. capsularis a new cardiac monoglycoside – corchoroside A – the aglycon of which proved to be strophanthidin. Somewhat later, the chemical nature of the sugar part of corchoroside A was clarified [5], and its complete structural formula was proposed. Recently, N. K. Abubakirov, V. A. Maslennikova, and M. B. Gorovits [7,8] isolated from the seeds of the long-pod jute a new cardiac triglycoside –olitoriside– from which was obtained by hydrolysis an aglycon which was shown to be strophanthidin; the nature of the sugar part was not established.

We too have been occupied with the study of the glycoside composition of long-pod jute seeds from plants of native origin. From the fermented seeds were obtained corchoroside A, its aglycon, strophanthidin, and a sugar, bovinose, the properties of which were identical with those previously described.

During our study of the glycoside composition of the unfermented seeds, we were able to establish the presence of, chiefly, two water-soluble glycosides, which are indicated* by spots "E" and "D" on the paper chromatograms; there were also found insignificant amounts of two substances, indicated by spots "C" (corchoroside A) and "B" (strophanthidin), which were evidently formed as a consequence of hydrolysis of the water-soluble glycosides during treatment of the extracts (see Figure 1).

In the preparation of the glycosides, the powdered seeds were extracted with dilute alcohol, and the extract was purified with $Pb(OH)_2$ and ether and then treated with a mixture of chloroform and alcohol (2:1) until the aqueous phase gave a negative Legal test. The residue obtained after concentration of the alcohol–chloroform extract was chromatographed on aluminum oxide. Elution was carried out with chloroform and then with chloroform containing 2-3 % alcohol. From the column separation was obtained a fraction (which gave only the single spot "D" on the paper chromatogram) from which was isolated in the crystalline state a new cardiac monoglycoside which we have named "olitorin". The main physicochemical properties of olitorin are presented in Table 1.

In order to determine the chemical structure of olitorin, it was hydrolyzed; an aglycon – olitorigenin – (Table 1) was obtained from the neutral part of the hydrolyzate, while from the aqueous acid part was obtained a crystalline 2-desoxy sugar. The latter compound crystallized readily from acetone-ether solution. It gave a positive Keller–Kiliani reaction. It melted at 98-102° C; R_f = 0.40 [in the system toluene-butanol-water (1:9:2)]; $[\alpha]_D^{19} = -16.20°$ (C = 1.111 in acetone).

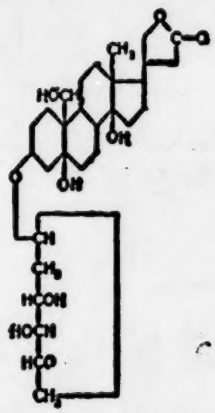
* For the sake of comparability of results of the paper-chromatographic investigation, we have used the symbols and systems previously used for this purpose by other authors [6].

TABLE 1

Properties of the Major Glycosides and Aglycons of the Long-Pod Jute

Expt. No.	Substance	Molecular formula	M.p.	$[\alpha]_D$
1	Olitorisside [7,8]	$C_{31}H_{52}O_{14}$	204—206° 222—224°	—4,5° (methanol)
2	Corchoroside A	$C_{29}H_{48}O_9$	160—165°	+13,41° (methanol)
3	Olitorin	$C_{29}H_{44}O_8$	157—162°	+18,18° (alcohol)
4	Olitorigenin (=strophanthidol)	$C_{23}H_{34}O_6$	218—125°	—
5	Strophanthidin	$C_{23}H_{32}O_6$	138—142° 177—178° 220—230°	+44,0° (methanol) +40,8° (alcohol)

Fig. 1. Chloroform: formamide-acetone (1:3), 17° C; 3 hours; 1) amorphous product (from the unfermented seeds); 2) corchoroside A; 3) olitorisside; 4) strophanthidin; 5) olitorin; 6) olitorigenin.



2.83 mg of the substance gave 4.99 mg of CO_2 and 2.07 mg of H_2O; mol. wt. 148.15.

Found %: C 48.11; H 8.18 $C_6H_{12}O_4$. Calculated %: C 48.63; H 8.17.

The properties of the substance, a mixed melting point, and the paper chromatography data all indicated that our sugar was bovinose.

In contrast to corchoroside A, the u. v. absorption spectrum of olitorin had only a single maximum, at about 220 mμ ($\log \varepsilon$ 4.38), and no maximum characteristic of a carbonyl group; i.e., olitorin does not have an aldehyde group at C_{19}.

We assumed that olitorigenin must differ from strophanthidin only by the presence of an alcohol group at C_{19}. In order to confirm this assumption, the aldehyde group of strophanthidin (which we had prepared earlier by hydrolysis of corchoroside A) was reduced by means of $NaBH_4$ to an alcohol group; it was demonstrated that the product was strophanthidol. The properties of the latter, a mixed melting point with olitorigenin, and paper chromatography data obtained in various solvents all showed that the compound was identical with olitorigenin. Having determined the chemical nature of the aglycon and sugar parts of olitorin, we propose the adjacent structural formula (I).

For purposes of comparison, we also carried out a paper chromatographic investigation of the glycosides and aglycons, including olitorisside*, which we obtained from the seeds of the long-pod jute. As may be seen from the figure, olitorin and olitorigenin differ from the glycosides and aglycons first isolated from long-pod jute by other authors.

SUMMARY

1. A new cardiac monoglycoside, which we have named olitorin, was isolated from the seeds of long-pod jute. It was established that olitorin is a bovinoside of strophanthidol.

2. The main glycosides of long-pod jute (which is cultivated in the

* Our thanks are due N. K. Abubakirov, V. A. Maslennikova, and M. B. Gorovits for presenting us with a sample of olitorisside.

Soviet Union) are: olitoriside, olitorin, and corchoroside A; the aglycons are: strophanthidin and strophanthidol.

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* Original Russian pagination. See C.B. Translation.

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THE ADDITION OF ALKYLSULFENYL CHLORIDES TO DERIVATIVES OF ACRYLIC ACID

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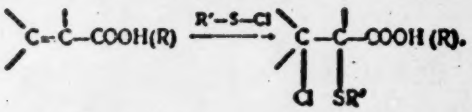
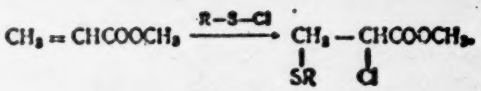
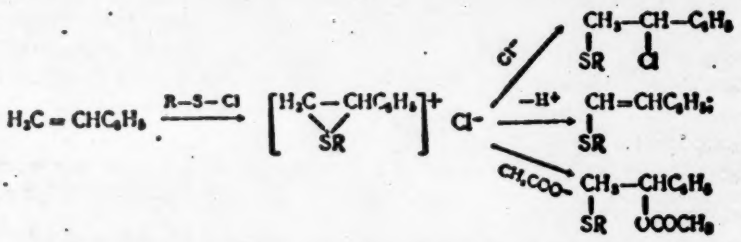
We have previously shown that alkylsulfenyl chlorides readily add to acrylic acids and their derivatives in conformity with the polarity of the starting materials with the formation of α-alkylmercapto-β-chloro-substituted acids of the type [1]:



Therefore, it appeared to be necessary to check the data presented in a paper by Brintzinger [2] in which the author described the products of the addition of alkylsulfenyl chlorides to methyl acrylate as α-chloro-β-alkylmercapto derivatives of propionic acid



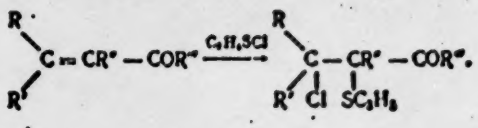
The author assigned this structure to the products in spite of a detailed investigation by him of the reaction of sulfenyl chlorides with compounds containing a labile hydrogen atom, such as malonic ester, acetoacetic ester, hydrogen sulfide, hydrogen cyanide, etc.; the data obtained in this investigation confirmed the generally accepted polarization of sulfenyl chlorides as R—S→Cl. Kharasch, studying the addition of 2,4-dinitrobenzenesulfenyl chloride to olefins, showed that the addition proceeds in accordance with Markownikoff's rule in conformity with the polarization of sulfenyl chlorides, in which the negative charge is centered on the chlorine atom [3]. Analyzing the results of a kinetic study of the addition of sulfenyl chlorides to olefins, the author proposed the following reaction mechanism [4]:



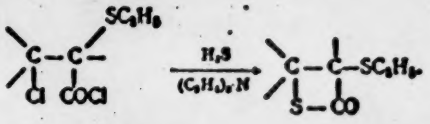
whence, depending on the reaction conditions, either the preferential formation of one of the three compounds or the simultaneous formation of all three is possible.

Our further investigations of the addition of sulfenyl chlorides to acrylic acid derivatives again confirmed

our previous proposal and controverted the data of Brintzinger. It was found that the addition of ethanesulfenyl chloride to acrylic, methacrylic, and dimethylacrylic acids, to acrylonitrile, to dimethylacryloyl chloride, and to ethyl dimethylacrylate proceeds with the formation of α-alkylmercapto-β-chloro derivatives of propionic acid:



The ethanesulfenyl chloride added very readily to the ester, more difficultly to the acids and the nitrile, and most difficultly to the acid chloride [1]. The corresponding β-propiothiolactones were obtained from the acid chlorides of the α-alkylmercapto-β-chloro derivatives of propionic acid and hydrogen sulfide [5]:



Were the course of the addition of sulfenyl chlorides otherwise, the formation of β-propiothiolactones would be impossible. The action of bases on the ethyl ester of β, β-dimethyl-β-chloro-α-ethyl-mercaptopropionic acid led to the elimination of hydrogen chloride and the formation of the ethyl ester of β, β-dimethyl-α-ethylmercapto-acrylic acid.

In 1958, Gundermann, by addition of mercaptan to the methyl ester of α-chloroacrylic acid, actually obtained the methyl ester of α-chloro-β-ethylmercaptopropionic acid [6]:

$$CH_2 = CClCOOCH_3 \xrightarrow{C_2H_5SH} C_2H_5SCH_2 - CHClCOOCH_3.$$

The boiling point of the methyl ester of α-chloro-β-ethylmercaptopropionic acid obtained in this manner was in agreement with the boiling point of the preparation obtained by Brintzinger by the addition of ethanesulfenyl chloride to methyl acrylate. On this basis and without sufficient grounds, Gundermann agreed with Brintzinger that during the action of sulfenyl chlorides on acrylic systems, the alkylmercapto group adds to the β-position and the chlorine atom adds to the α-position. In order to clear up this question once and for all, we carried out special syntheses of α-chloro-β-ethylmercaptopropionitrile (I) and α-ethylmercapto-β-chloropropionitrile (II) and compared their properties. I was prepared by the addition of ethyl mercaptan to α-chloroacrylonitrile:

$$CH_2 = CClCN \xrightarrow{C_2H_5SH} C_2H_5S - CH_2 - CHClCN,$$

and II was obtained by the addition of ethanesulfenyl chloride to acrylonitrile:

$$CH_2 = CHCN \xrightarrow{C_2H_5SCl} CH_2ClCH(SC_2H_5)CN.$$

It was found that the two compounds have the same boiling point and closely similar refractive indices and densities, but that they differ sharply in chemical properties. Thus, I remained unchanged during prolonged storage; even the action of sodium acetate in methanol at room temperature did not split out hydrogen chloride. However, II spontaneously lost hydrogen chloride during storage (acid reaction to congo indicator, change in refractive index), and with sodium acetate under the same conditions as I, almost all of the II underwent elimination of hydrogen chloride with the formation of the β-alkylmercaptoacrylonitrile. The infrared spectra of compounds I and II also differed (see Figures 1 and 2).

Thus, it is quite clear that the negative charge in alkylsulfenyl chlorides is centered at the chlorine atom and that alkylsulfenyl chlorides add to acrylic systems in conformity with the indicated polarization, forming α-alkylmercapto derivatives.

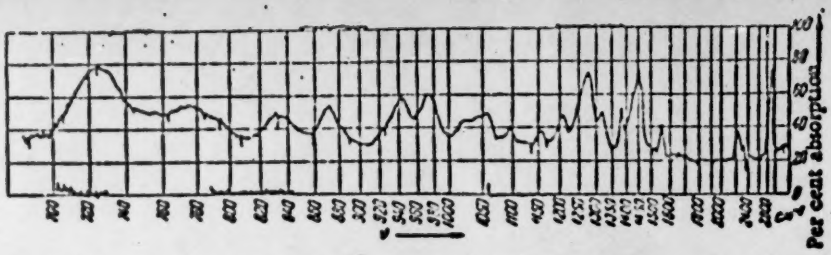


Fig. 1. I.r. spectrum of α-chloro-β-ethylmercaptopropionitrile (I).

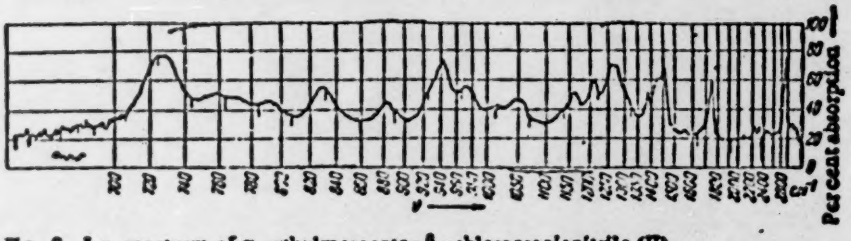


Fig. 2. I.r. spectrum of α-ethylmercapto-β-chloropropionitrile (II).

EXPERIMENTAL PART

α-Methyl-α-ethylmercapto-β-chloropropionyl chloride. 9.65 g (0.1 mole) of ethanesulfenyl chloride was added to 8.6 g (0.1 mole) of methacrylic acid in 30 ml of CCl_4, during which the reaction mixture was cooled with water; the reaction mixture was allowed to stand at room temperature for 2 hours, and was then heated on a water bath with 36 g (0.3 mole) of thionyl chloride. There was obtained 14 g of α-methyl-α-ethylmercapto-β-chloropropionyl chloride, b.p. 110°/5-6 mm, n_D^{20} 1.5097, density 1.23%.

Found %: C 35.18; H 4.74 $C_6H_{10}Cl_2OS$. Calculated %: C 35.8; H 4.97.

α-Ethylmercapto-β-chloropropionitrile. 9.65 g (0.1 mole) of ethanesulfenyl chloride was added to 5.3 g (0.1 mole) of acrylonitrile in 25 ml of absolute ether, and the mixture was allowed to stand at room temperature until the following day. The solvent was evaporated, and 10 g, 75% yield, of α-ethylmercapto-β-chloropropionitrile was obtained; b.p. 89-90°/5-6 mm, n_D^{20} 1.5063, density 1.171; MR, found 38, calculated 37.95.

Found %: C 39.96; H 5.03 C_5H_8NSCl. Calculated %: C 40.20; H 5.35.

β,β-Dimethyl-β-chloro-α-ethylmercaptopropionyl chloride. 10 g(0.1 mole) of ethanesulfenyl chloride in 25 ml of CCl_4 was added to 10 g (0.1 mole) of dimethylacrylic acid in 25 ml of CCl_4. The mixture was allowed to stand until the following day. 36 g (0.3 mole) of thionyl chloride was then added, and the mixture was heated on a water bath until the evolution of SO_2 and HCl had ceased. The β,β-dimethyl-β-chloro-α-ethylmercaptopropionyl chloride was obtained in 72 % yield; b.p. 92-93°/5-6 mm.

5 g of ethanesulfenyl chloride was added, under the same conditions, to 6 g of dimethylacryloyl chloride. Complete decolorization of the sulfenyl chloride was not observed, even on prolonged heating of the mixture; the yield of β,β-dimethyl-β-chloro-α-ethylmercaptopropionyl chloride did not exceed 30 %.

Found %: C 39.19; H 5.46 $C_7H_{12}OCl_2S$. Calculated %: C 39.07; H 5.58.

Ethyl ester of β,β-dimethyl-α-ethylmercaptoacrylic acid. 5.7 g (0.03 mole) of the ethyl ester of β,β-dimethyl-β-chloro-α-ethylmercaptopropionic acid was dissolved in 10 ml of methyl alcohol, and 20 ml of a 2 N solution of NaOH in methyl alcohol was added dropwise. The alkaline reaction immediately disappeared. After evaporation of the alcohol, the residue was dissolved in ether, and the ether solution was washed with water and dried over magnesium sulfate. 3 g of the ethyl ester of β,β-dimethyl-α-ethylmercaptoacrylic acid was obtained. B.p. 115-116°/15 mm.

Found %: C 57.29; H 8.60; S 17.35 $C_9H_{16}O_2S$. Calculated %: C 57.44; H 8.51; S 17.02.

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INVESTIGATION OF PHENYL-RADICAL TRANSFER REACTIONS

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In work previously reported [1], we made use of phenyl-radical exchange with benzene for proof of the appearance of free phenyl radicals in certain radical processes. The existence of such an exchange, which proceeds by an "express" reaction, can be detected by means of labeled compounds:

$$C_6H_5^{\bullet} + C_6H_6 - C_6H_6^{\bullet} + C_6H_5^{*}.$$

It has also been noted, by this same means, that interaction of the radicals with the solvent does not always take place. In the presence of finely divided metals, the radicals can react with each other on the surface of the metal and not transfer into the bulk of the solvent.

In the present work, we investigated the decomposition of some compounds yielding phenyl radicals (nitroso-acetanilide, diphenyliodonium iodide, the double salt benzenediazoniumzinc chloride) in solution in labeled benzene in the presence of metallic mercury.

It is well known that in the presence of mercury, nitrosoacetanilide in carbon tetrachloride solution forms phenylmercury chloride [2]. We carried out this reaction in a medium of benzene labeled with C^{14}. A weighed sample of the nitroso derivative (5.5 g) in solution in labeled benzene (32 g, activity 825 imp /minute) was vigorously agitated with mercury (20 g) at 35-40° for 4 hours. The nitrosoacetanilide reacted chiefly with the benzene. The resulting biphenyl (1.5 g, 58% yield) consisted of phenyl radicals from both the nitroso compound and the benzene (the activity of the biphenyl was 373 imp /minute; i.e., 45% of the phenyl radicals came from the benzene). However, interaction of the phenyl radicals with mercury occurred to some extent.

The phenyl mercury acetate obtained from the reaction was converted to the chloride, which, after repeated recrystallization (0.15 g was recovered), proved to be inactive. When nitrosoacetanilide was decomposed in the presence of freshly reduced copper in a medium of C^{14}-labeled benzene, no essential change in the isotope composition of the resulting biphenyl was observed.

Analogous results were obtained with diphenyliodonium iodide. As Reutov and co-workers have shown [3], organomercury compounds are readily prepared drom diphenyliodonium salts and mercury in various media. We carried out this reaction by vigorously agitating diphenyliodonium iodide (4 g) in labeled benzene (40 g, activity 1026 imp /minute) with mercury (10 g) at 80° for 24 hours; 1.2 g (15% yield) of phenylmercury iodide was isolated from the reaction mixture, and this was found to be practically inactive. The iodobenzene obtained under these conditions (2.4 g, 60% yield) was also inactive.

Thus, the solvent, benzene, does not participate in the reaction. The phenylmercury iodide was formed from diphenyliodonium iodide and not from iodobenzene, which was formed by decomposition of the diphenyliodonium iodide. This was also confirmed by a control experiment which showed that phenylmercury iodide is not formed from iodobenzene and mercury under these conditions. Photodecomposition (irradiation with a PRK-2 lamp for 180 hours) of diphenyliodonium iodide (2 g) in C^{14}-labeled benzene (45 g, activity 1470 imp /minute) gave biphenyl (0.15 g, 20% yield) and iodobenzene (0.49 g, 24% yield). The biphenyl had an activity of 3165 imp /minute, i.e., 47% of the activity of the original benzene, while the iodobenzene was almost inactive.

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* As in the Russian original - Publisher's note.

TABLE 1

Reaction of $(C_6H_5N_2)_2ZnCl_4$ with Benzene at 80° for 10 Hours

Expt. No.	Taken in the reaction				Obtained from the reaction						
		Benzene			Chlorobenzene			Biphenyl			
	$(C_6H_5N_2)_2ZnCl_4$	g	Activity, imp/min	Metal added, g	g	yield, %	activity, imp/min	g	formed, %	activity, imp/min	Phenyl radicals from benzene, %
1	10	35	220	—	1.9	35.5	None	0.18	10.0	120	41.4
2	10	35	632	2Hg	2.0	37.2	None	0.19	10.5	247	39.6
3	10	35	452	2Hg	2.1	39.1	None	0.19	10.5	172	38.2
4	10	35	—	30 g (Hg) Na	2.1	39.1	None	0.15	8.1	—	—
5	10	35	220	3Zn	1.9	35.5	None	0.18	10.0	117	40.2
6	10	35	275	1.5Cu	1.8	33.5	None	0.13	7.9	118	42.5

A preliminary experiment confirmed that radiation-induced exchange of phenyl radicals does not take place between iodobenzene (4 g) and benzene (15 g, activity 1000 imp /minute). The iodobenzene remained inactive after irradiation for 160 hours.

The last example was the decomposition of the double salt $(C_6H_5N_2)_2ZnCl_4$ in a medium of labeled benzene at 80° (Table 1).

The main product of this reaction was chlorobenzene, which was practically inactive after careful purification. In addition, a small amount of biphenyl was obtained. The isotope composition of the latter established that it was formed from phenyl radicals from both benzene and the benzenediazonium compound.

In order to solve the problem of whether free radicals are formed during the process, we carried out the decomposition of the diazonium double salt in the presence of metallic mercury (Experiments 3 and 4). However, we were unable to detect the formation of phenyl mercury compounds. Precisely the same negative results were obtained when sodium amalgam was substituted for mercury (Experiment 4).

We had assumed that the sodium, by combining with the chlorine, would increase the yield of phenyl radicals. As the experimental data showed, the addition of either mercury or sodium amalgam had absolutely no effect on the yield of chlorobenzene and biphenyl.

Similarly, the addition of metallic zinc (Experiment 5) or copper (Experiment 6) had no effect on the decomposition of the diazonium double salt in benzene.

Thus, the appearance of free phenyl radicals was not detected in any of our experiments.

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COPOLYMERIZATION OF UNSATURATED ACYL DERIVATIVES OF BUTYL POLYTITANATE WITH STYRENE

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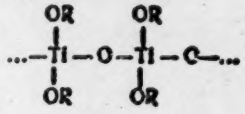
(Presented by Academician B. A. Kazanskii, March 5, 1959)

Among polymeric titanium-containing compounds, the best studied are the polymers obtained by means of hydrolysis or polycondensation of esters of orthotitanic acid and containing an inorganic chain consisting of titanium and oxygen atoms, the chain being framed by organic groups:



(I)

Titanium-containing polymers obtained by polymerization of unsaturated organotitanium compounds or by copolymerization of these compounds with vinyl monomers have been studied to a considerably lesser extent. There are patent data [1-3] concerning the possibility of copolymerizing unsaturated esters of orthotitanic acid and also of alkoxytitanium acylates of the formula $(RO)_nTi(OCOR')_{4-n}$, containing unsaturated acyl groups with unsaturated monomers. Vinyl esters of orthotitanic acid such as divinyldiisopropyl titanate $(i\text{-}C_3H_7O)_2Ti(OCH=CH_2)_2$, tetrastyryl titanate $Ti(OCH=CHC_6H_5)_4$, and others, which may be obtained by the interaction of alkyl orthotitanates with enolizable aldehydes or ketones [4], polymerize readily. These samples exhaust the available literature information on the polymerization and copolymerization of organic titanium compounds.

As may be seen from the information presented above, up to the present, studies of polymerization and copolymerization reactions have been confined to monomeric organotitanium compounds (i.e., compounds containing only one titanium atom in the molecule). It seemed to us to be of interest to explore the possibility of the copolymerization, with vinyl monomers, of titanium-containing polymers of the type of (I) in which the framing groups are unsaturated. The literature contains no data on the synthesis and copolymerization of such compounds.

For the preparation of unsaturated polycondensation products of type (I), we made use of the ready substitution of the alkoxy group in alkyl polytitanates by acyl radicals. As was shown by Boyd [5], when an alkyl polytitanate is heated under vacuum with an aliphatic acid, preferably one with a long chain, replacement of alkyl groups by acyl groups takes place and the corresponding alcohol is liberated:

$$(RO)_{2(n+1)}Ti_nO_{n-1} + mR'COOH \rightarrow (R'COO)_m(RO)_{2(n+1)-m}Ti_nO_{n-1} + mROH \qquad (II)$$

By carrying out such a reaction between butyl polytitanate (with an average degree of polycondensation of n = 12) and cinnamic acid, $C_6H_5CH=CHCOOH$, or furylacrylic acid, $C_4H_3OCH=CHCOOH$, at various ratios of reactants, we obtained acyl derivatives of type (II) with ratios of R'COO/Ti of 13/12 and 6/12 in experiments with cinnamic acid and of 12/12 and 6/12 in experiments with furylacrylic acid. Depending on the amount of acid introduced, these products were waxy or resinous substances. When heated with styrene at 100-150° in the presence of 1-2% benzoyl peroxide, these compounds underwent copolymerization with the styrene, forming transparent red-brown polymers. These polymers are not soluble in such solvents as acetone, benzene, or toluene; they swell in benzene or toluene. An interesting fact is the stability of these polymers toward the action of water.

In contrast to butyl polytitanate and its acyl derivatives, these polymers do not undergo visible change on prolonged storage (up to three months) in water, under the influence of boiling water, or when heated with aqueous acetone.

By way of example, we present below the preparation of the unsaturated product of the condensation of butyl polytitanate (n = 12) with cinnamic acid in which the ratio $C_6H_5CH = CHCOO/Ti = 13/12$ and the copolymerization of this substance with styrene.

EXPERIMENTAL PART

The initial butyl polytitanate was prepared by hydrolysis of butyl orthotitanate, $Ti(OC_4H_9)_4$, in butyl alcohol [6]. To a solution of 36.7 g (1 mole) of butyl orthotitanate in 100 ml of anhydrous butyl alcohol was slowly added with vigorous stirring, a solution of 1.85 g (0.95 mole) of water in 40 ml of butyl alcohol. After all of the solution had been added, the reaction mixture was heated, with stirring, for an hour at 60-65° (bath temperature), after which the solvent was distilled (finally under a vacuum of 5 mm and a temperature of 180°). The resulting very viscous, yellowish-green transparent polymer had an average degree of polycondensation, "n", equal to 12.

Found %: TiO_2 36.28; 36.29 $(C_4H_9O)_{26}Ti_{12}O_{11}$. Calculated %: TiO_2 36.23.

12 g of this butyl polytitanate was mixed with 8.7 g of cinnamic acid (m.p. 133°) and the mixture was heated at 150° and 15-20 mm pressure. The butyl alcohol which distilled was collected in a cold trap; practically the theoretical amount (4.2 g) of butyl alcohol was collected. Final removal of the alcohol was carried out by heating at 150-160° and 2 mm pressure. The resulting product was a resinous substance, soluble in organic solvents. According to the analytical data, it contained 13 cinnamic acid residues for each 12 titanium atoms.

Found %: Ti 15.85; 15.89; C 55.88; 56.05; H 5.70; 5.77 $(C_4H_9O)_{13}(C_6H_5CH = CHCOO)_{13}Ti_{12}O_{11}$. Calculated %: Ti 15.95; C 56.13; H 5.76.

2 g of this product was dissolved in 3 ml of styrene, 1-2% of benzoyl peroxide was added, and the mixture was heated in a hood at 100° for several days; this resulted in the formation of a solid, transparent polymer with a reddish-brown color. When the copolymerization was carried out at 140-150°, the mixture lost its fluidity after only 2 hours, and it completely solidified within 2-3 days. The resulting polymer was not hydrolyzed by water or aqueous acetone, and did not dissolve in acetone, benzene, or toluene. By extracting the polystyrene and unreacted starting materials with toluene, and drying and analyzing the residue it was shown that this substance was a copolymer, and not a product of the further condensation of titanium compounds.

Found %: Ti 9.68; 9.73; C 73.31; 74.14; H 5.79; 5.80

These data demonstrate the possibility of preparing copolymers based on vinyl monomers and polytitanoxane compounds containing unsaturated organic groups.

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A NEW METHOD FOR THE SYNTHESIS OF AROMATIC ORGANOSILICON MONOMERS*

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The following methods have become well known and widely used for the synthesis of aromatic organosilicon monomers: a) substitution of an aryl radical for a chlorine atom or RO group by the action of organometallic compounds on chloro- and alkoxysilanes, b) the direct action of aryl halides on silicon-containing contact masses (direct synthesis), and c) the interaction of silicon hydrides with aromatic compounds at elevated temperatures (200-500°) and pressures (either in the presence or absence of a catalyst) [1-4]: $\geq SiH + C_6H_6 \rightarrow \geq SiC_6H_5 + H_2$. The reaction of silicon hydrides with aryl chlorides in the presence of a catalyst, in accordance with the last-mentioned method, can proceed in two directions [5]:

$$ClC_6H_5 + \geq Si-H \begin{cases} \rightarrow \geq SiC_6H_4Cl + H_2 & (I) \\ \rightarrow \geq SiC_6H_5 + SiCl_4 + H_2 & (II) \end{cases}$$

When the reaction is carried out without a catalyst (t = 400-500°; p = 5-7.5 atm), it proceeds only according to scheme (II) [1]. In all patents devoted to this reaction, it is emphasized that at least part of the reaction mixture should be in the liquid phase. Only two patents [6, 7] are directed to conducting the reaction in the gas phase, and in both of these it is stated that it is necessary to use a catalyst (copper or palladium) in carrying out the reaction. The data in these two patents as well as the increase in the yield of phenyltrichlorosilane resulting from the direct synthesis when a mixture of chlorobenzene and HCl [8] (the latter forms $HSiCl_3$ with the Si) or a mixture of chlorobenzene and $HSiCl_3$ [9] is employed show that the reaction $HSiCl_3 + ClC_6H_5 \rightarrow Cl_3SiC_6H_5 + HCl$ occurs principally in the gas phase.

And, indeed, we have observed that with an increase in the temperature of the reaction zone to 550-700°, aryl chlorides readily condense with silicon hydrides at atmospheric pressure in the gas phase:

$$RCl + HSiR'_nCl_{3-n} \rightarrow RR'_nSiCl_{3-n} + HCl,$$

where R is an aromatic radical, R' is CH_3 or C_2H_5, and n=0,1.

The reaction was carried out by passing a mixture of the aryl chloride and silicon hydride through a heated empty quartz tube. The tube used in the work had a diameter of ~10 mm and a heated zone 150 cm long. The use of catalysts or even of ceramic or glass packing led to a decrease in the yields of condensation products.

The condensate was distilled in a column equivalent to 40 theoretical plates. As an example of the analytical methods used, the analysis of the condensate obtained during the preparation of phenyltrichlorosilane from chlorobenzene and trichlorosilane was carried out as follows. Fraction I (b.p. 31-33°) was trichlorosilane. Fraction II

* A brief account of the method has been published in reference [10].

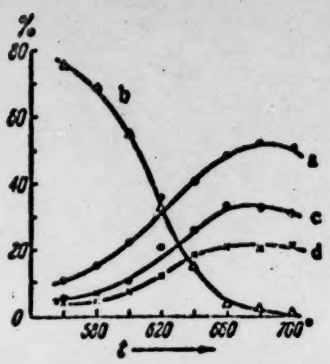

Fig. 1. Temperature dependence of the degree of $HSiCl_3$ conversion and of the yields of condensation products; contact time $\tau = 15.7$ seconds; C_6H_5Cl/ /$HSiCl_3$ = 2/1; a) $C_6H_5SiCl_3$; b) $HSiCl_3$; c) $SiCl_4$; d) C_6H_6.

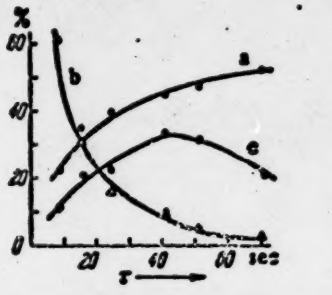

Fig. 2. Effect of contact time on the degree of $HSiCl_3$ conversion and on the yields of $C_6H_5SiCl_3$ and $SiCl_4$; temperature of reaction zone, 620°; C_6H_5Cl/ /$HSiCl_3$ = 2/1. a) $C_6H_5SiCl_3$; b) $HSiCl_3$; c) $SiCl_4$.

(b.p. 33-35°) was a mixture of trichlorosilane and $SiCl_4$; the amount of $HSiCl_3$ in this fraction was determined from the active hydrogen and the remainder was taken as $SiCl_4$. Fraction III (b.p. 55-58°) consisted of $SiCl_4$. Fraction IV (b.p. 58-78°) was a mixture of $SiCl_4$ and benzene; the $SiCl_4$ content of the fraction was determined from the hydrolyzable chlorine. Occasionally, an analysis of the entire fraction boiling up to 80° was carried out. $HSiCl_3$ was determined from the active hydrogen; the $SiCl_4$ was determined from the hydrolyzable chlorine taking into account the $HSiCl_3$, and the remainder consisted of benzene. Both methods gave practically equivalent results. The fraction boiling over the range 80-132° was a mixture of benzene and chlorobenzene; the amount of chlorobenzene was estimated from the density of the mixture. The fraction boiling over the range 134-199° was a mixture of chlorobenzene and phenyltrichlorosilane; the amount of the latter was estimated from the amount of hydrolyzable chlorine. The fraction boiling at 199-202° consisted of phenyltrichlorosilane. Analyses of the other condensates were carried out in a similar manner.

Using the reaction in which phenyltrichlorosilane is formed, $HSiCl_3 + ClC_6H_5 \rightarrow Cl_3SiC_6H_5 + HCl$, we studied the effects of temperature of the reaction zone, contact time, and ratio of starting materials on the degree of conversion of $HSiCl_3$ and on the yields of condensation products. The effect of the temperature in the reaction zone is shown in Figure 1.

The presence in the reaction products of significant amounts of $SiCl_4$ and benzene shows that in addition to the basic reaction yielding phenyltrichlorosilane, the interaction of $HSiCl_3$ and C_6H_5Cl proceeds by another route with the formation of silicon tetrachloride and benzene: $HSiCl_3 + C_6H_5Cl \rightarrow SiCl_4 + C_6H_6$. However, silicon tetrachloride was always obtained in greater molar amounts than was benzene; i.e., it was also formed by still another route. Analysis of the gaseous reaction products showed that they consisted almost entirely of HCl and H_2. The molar amount of hydrogen corresponded to the molar excess of $SiCl_4$ over benzene as would be required by the reaction $4HSiCl_3 \rightarrow 3SiCl_4 + Si + H_2$. Thus, along with the interaction of $HSiCl_3$ and C_6H_5Cl, pyrolysis of $HSiCl_3$ also occurred, and, for example, at 700° about 10% of the original trichlorosilane underwent pyrolytic cleavage. The presence in the gaseous reaction products of only insignificant amount of methane, ethane, ethylene, propane, propylene, butane, butene, and amylenes, and the insignificant deposition of carbon on the walls of the reaction tube indicated that pyrolysis of the chlorobenzene took place to only a slight extent. The effect of contact time on the completeness of conversion of trichlorosilane and on the yields of $SiCl_4$ and $C_6H_5SiCl_3$ is shown in Figure 2.

An increase in contact time promoted smoother conversion of the trichlorosilane and, therefore, an increase in the yield of $C_6H_5SiCl_3$. It was found that the maximum yield of $C_6H_5SiCl_3$ (52%) was the same at different temperatures, but it was obtained at 680° at $\tau = 15.7$ seconds and at 620° at $\tau = 70$ seconds. Naturally, when operating at maximum yield, decreasing the temperature of the reaction zone decreases the productivity of the apparatus. Figure 3 shows that the optimum ratio of chlorobenzene to trichlorosilane is 2/1. An increase in the ratio from 2/1 to 3/1 had practically no effect on the yield of phenyltrichlorosilane, but it led to an increase in the amount of silicon tetrachloride formed.

Upon consideration of the results obtained, we carried out an investigation of the optimum reaction temperature for the synthesis of phenylmethyldichlorosilane: $CH_3SiHCl_2 + C_6H_5Cl \rightarrow CH_3SiCl_2C_6H_5 + HCl$. The ratio of chlorobenzene to methyldichlorosilane was set at 2/1 and the contact time at $\tau = 30$ seconds; these conditions gave a sufficiently high productivity.

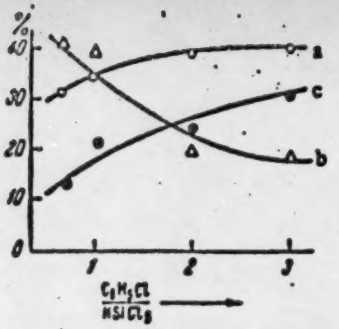

Fig. 3. Effect of changes in the ratio of starting materials, C_6H_5Cl on the degree of $HSiCl_3$ conversion and on the yields of $C_6H_5SiCl_3$ and $SiCl_4$. Temperature of the reaction zone, 620°. Contact time, τ = 23.6 seconds. a) $C_6H_5SiCl_3$; b) $HSiCl_3$; c) $SiCl_4$.

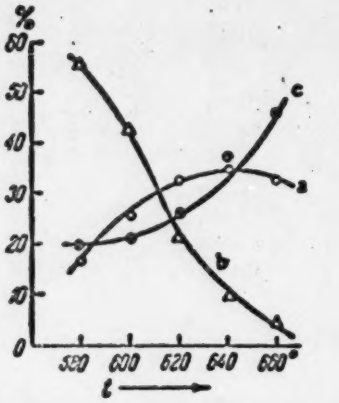

Fig. 4. Effect of temperature of the reaction zone on degree of CH_3SiHCl_2 conversion and on the yields of $C_6H_5SiCH_3Cl_2$ and CH_3SiCl_3; C_6H_5Cl / /CH_3SiHCl_2=2/1; contact time, τ=30 seconds. a) $C_6H_5SiCH_3Cl_2$; b) CH_3SiHCl_2; c) CH_3SiCl_3.

It was found that the interaction of chlorobenzene with methyldichlorosilane proceeded primarily by the same routes as the interaction with trichlorosilane. Paralleling the reaction yielding phenylmethyldichlorosilane was a reaction yielding benzene and methyltrichlorosilane: $CH_3SiHCl_2 + C_6H_5Cl \rightarrow CH_3SiCl_3 + C_6H_6$. The occurrence in the gaseous reaction products of a significant amount of hydrogen and the deposition of silicon on the walls of the reaction tube indicated that, similarly to the case of $HSiCl_3$, pyrolysis of CH_3SiHCl_2 took place. An increase in the temperature of the reaction zone to above 650° led to appreciable formation of $C_6H_5SiCl_3$, along with the $C_6H_5SiCH_3Cl_2$ (there was no appreciable formation of $C_6H_5SiCl_3$ at 640°, while at 660°, it comprised up to 10% of the weight of the $C_6H_5SiCH_3Cl_2$ formed). These results are presented in Figure 4. The maximum yield of phenylmethyldichlorosilane was obtained at 640° and amounted to 35%.

Thus, the method of preparing phenyltrichlorosilane and phenylmethyldichlorosilane by high-temperature condensation of silicon hydrides with chlorobenzene is preferable to the method in which silicon hydrides are condensed with aromatic compounds in the liquid phase, not only with respect to simplicity of apparatus, but also because higher yields of the desired compounds are obtained.

The high-temperature condensation was extended to other aryl chlorides, in particular, to α-chloronaphthalene and p-dichlorobenzene. At 640°, the yields of naphthyltrichlorosilane and naphthylmethyldichlorosilane were, respectively, 60% and 50%. That the yields of naphthylchlorosilanes were higher than those of the corresponding phenylchlorosilanes merits attention. Moreover, it was found in the case of the synthesis of naphthylchlorosilanes, silicon tetrachlorides was formed to a considerably lesser extent than in the case of phenylchlorosilane synthesis; the formation of naphthalene was also insignificant.

p-Dichlorobenzene was also successfully condensed with silicon hydrides in the gas phase. Thus, at 640°, at a contact time of 30 seconds, and a ratio of $C_6H_4Cl_2$ to $HSiCl_3$ of 1/1, the yield of chlorophenyltrichlorosilane was 30%, while under the same conditions, the yield of chlorophenylmethyldichlorosilane was 20%. In both cases, reaction at both C — Cl bonds of the p-dichlorobenzene occurred to some extent with the formation of bis(chlorosilyl) benzenes. The yields of products cited in the present paper are based on the original silicon hydride.

The results presented in the present paper and also the successful extension of the condensation reaction to the condensation of silicon hydrides with a number of other RC_6H_4Cl leads us to assert that the high-temperature condensation of aryl chlorides with silicon hydrides in the gas phase is a new method for the synthesis of aromatic organosilicon monomers.

The high temperature of the reaction zone and also that the reaction was successfully carried out in an empty tube, i.e., with a minimum of surface area, compels the assumption that the reaction proceeds by a radical mechanism. The formation of different substances, for example, during the reaction of $HSiCl_3$ with C_6H_5Cl, can be represented by the following scheme:

$$HSiCl_3 \xrightarrow{\Delta} \dot{H} + \dot{S}iCl_3,$$

$$C_6H_5Cl + \dot{S}iCl_3 \rightarrow C_6H_5SiCl_3 + \dot{C}l,$$

$$\dot{C}l + HSiCl_3 \rightarrow HCl + \dot{S}iCl_3, \text{ etc.}$$

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HEATS OF COMBUSTION OF SOME BRANCHED ALKANES

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(Presented by Academician A. N. Nesmeyanov, April 13, 1959)

In contrast to other organic compounds, for many classes of hydrocarbons there is currently available a large amount of reliable experimental data on various physicochemical properties, in particular, heat of combustion.

The existence of this experimental material has permitted the development of additive schemes for the calculation of values of various physicochemical properties for those hydrocarbons for which experimental values are not available. The significance of such schemes does not require elaboration if one considers the enormous, continuously increasing number of hydrocarbons which are being synthesized. The accuracy with which one additive scheme or another can predict values of physicochemical properties of such substances depends, obviously, on the assumptions on which the scheme is based and on the care with which all interatomic and intermolecular interactions occurring in these substances are taken into account.

The simplest class of hydrocarbons is the alkanes, in which there are only ordinary C—C and C—H bonds. However, all of the C—H bonds cannot be considered equivalent with respect to the contributions made by these bonds to one physicochemical property or another. A scheme based on an assumption of bond equivalence would be very simple, but it obviously could not reflect differences in the physicochemical properties of isomers. Hence, more careful classification of C—C and C—H bonds is clearly required.

There is available at the present time a large number of additive schemes by which it is possible to calculate, with more or less accuracy, heats of combustion (and a number of other physicochemical properties) of the alkanes [1-10].

The most detailed approach is that employed by the scheme proposed by V. M. Tatevskii [5]. In this scheme, C—C bonds in alkanes are divided into ten subtypes according to whether the carbon atoms involved in a given bond are primary, secondary, tertiary, or quaternary. This approach takes into account the basic interactions of the atoms in alkane molecules with respect to bonds in which the atoms are not directly involved, and the calculated values reflect the experimental values with an accuracy which is not less than the accuracy of the experimental data.

Confining our attention to only heat of combustion in the liquid state at 25°, it may be pointed out that for 44 alkanes for which it is possible to compare values calculated by V. M. Tatevskii's scheme with experimental values, the average deviation is ± 0.5 kcal/mole. Sharp deviations of experimental [11] and calculated values are found in only three cases: 2,2,4-trimethylpentane (2.12 kcal/mole), 2,2,3,4-tetramethylpentane (1.77 kcal per mole), and 2,2,4,4-tetramethylpentane (5.22 kcal/mole). In all of these cases, the deviations can be explained on the basis that the method of calculation does not take into account interactions of substituents (methyl groups) located in the 2,2,4-positions (the interaction should be twice as great in the latter case). Taylor, Pignocco and Rossini [1] have pointed out that such interaction must exist; indeed, V. M. Tatevskii has repeatedly pointed out this phenomenon.

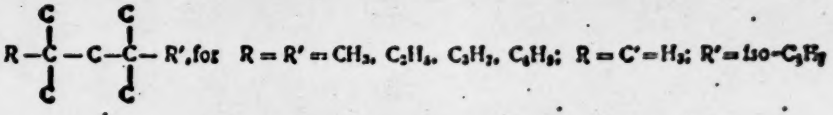
* L. V. Fedorchuk and I. Baukh participated in the work on the synthesis and purification of the alkanes investigated.

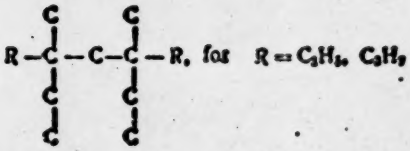
TABLE 1

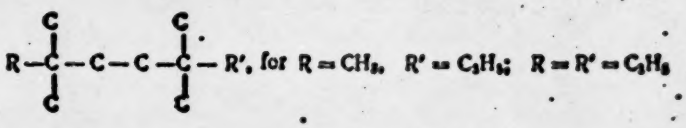
Substance	Heat of combustion in kcal/ mole		
	Experimental	Calculated	Δ
2,2,4,4-Tetramethylpentane	1462,2	1457,5	+4,7
3,3,5,5-Tetramethylheptane	1776,5	1772,0	+4,5
4,4,6,6-Tetramethylnonane	2090,4	2084,4	+6,0
5,5,7,7-Tetramethyldecane	2400,2	2396,9	+3,3
2,2,4,4,5-Pentamethylhexane	1775,7	1771,7	+4,0
3,5-Dimethyl-3,5-diethylheptane	2092,9	2086,5	+6,4
4,6-Dimethyl-4,6-diethylnonane	2401,7	2396,0	+5,7
2,2,5,5-Tetramethylheptane	1770,4	1770,9	−0,5
3,3,6,6-Tetramethyloctane	1927,6	1928,2	−0,6

Since there is available only one example of an alkane substituted in the 2,2,4,4-positions, and it is only in such an alkane that this deviation of calculated, from experimental, values can be noted, it appeared of interest to determine whether similar deviations would be observed in other alkanes having this grouping and whether the magnitude of these deviations would be constant or would depend on the structure of the rest of the molecule. Moreover, it was of interest to determine the heat of combustion of compounds in which quaternary carbon atoms are separated not by one, but by two methylene groups. For this structure, the calculated heat of combustion should agree with the experimental.

In this connection, the heats of combustion of hydrocarbons of the following structures were determined in the present work:

1)  for $R = R' = CH_3$, C_2H_5, C_3H_7, C_4H_9; $R = C' = H_3$; $R' = iso\text{-}C_3H_7$

2)  for $R = C_2H_5$, C_3H_7

3)  for $R = CH_3$, $R' = C_2H_5$; $R = R' = C_3H_7$

All of the compounds investigated were prepared by a double Grignard-Wurtz reaction. Details of the synthesis and the physicochemical constant of the substances synthesized have been published in part [12-14], and part will be published in the coming year. After synthesis, all of the compounds were carefully purified and distilled in a column. Following the distillation, each substance was chromatographed on silica gel.

Quantitative determination of purity by melting curves* was carried out for only two of the substances 2,-2,5,5-tetramethylheptane and 3,3,6,6-tetramethyloctane (the remainder of the compounds were glasses in the solid state, with the exception of 2,2,4,4-tetramethylpentane). The purity of these compounds was 99.4 ± 0.1 and 98.7 ± 0.2 mole per cent, respectively.

The method used for the determinations of the heat of combustion has been described previously [15]. The calorimeter constant was determined by combustion of standard benzoic acid. The isothermal heat of combustion of the benzoic acid at 20° was taken as 6319.0 calories per gram of acid weighed in vacuo (1 calorie = 4.1840 joules). The results had a precision of 0.02-0.4% (average deviation from the arithmetic average). For each

* The analyses were carried out in the A. G. Anikinyl Thermodynamics Laboratory of the chemical faculty of Moscow University.

substance, samples of different degrees of purity were burned, and the value of the heat of combustion was considered to be established only upon agreement of the results obtained from different samples.

Our experimental data are presented in Table 1. In one of the columns headed "heat of combustion" are given, in kcal /mole, the changes in enthalpy during isothermal combustion (at 25°) of the substances in the liquid state at a pressure of 1 atm., the reaction products being gaseous CO_2 and H_2O (also at a pressure of 1 atm).

In the other column headed "heat of combustion" are given the values of the heat of combustion of the corresponding compounds calculated by the method of V. M. Tatevskii. The Δ column gives the deviations of these values. As may be seen from this column, for all of the hydrocarbons containing in the molecule a grouping of two quaternary carbon atoms separated by one CH_2 group, the experimental heats of combustion differ from the values calculated by Tatevskii's method by an average of 5±1 kcal /mole. This value may be used to correct values calculated by Tatevskii's method for all alkanes containing this grouping.

As would be expected, in those cases where the alkane molecule contained a grouping of two quaternary carbon atoms separated by two CH_2 groups, the calculated values were in agreement with the experimental values within the limits of experimental error.

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ISOMERIZATION OF γ-OXIDES TO ALIPHATIC CARBONYL COMPOUNDS. THE EFFECT OF TEMPERATURE AND STRUCTURE OF THE COMPOUNDS

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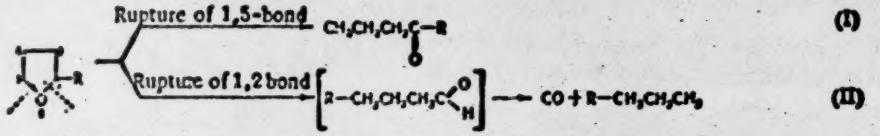
As we have previously shown [1], isomerization of γ-oxides (tetrahydrofurans) to aliphatic carbonyl compounds proceeds readily in the vapor phase over platinized carbon at the comparatively low temperature of 230-250°. When an alkyl group is present at the α-position of the tetrahydrofuran ring, cleavage of the ring proceeds predominantly at that C—O bond which is furthest removed from the alkyl radical (the 1,5-bond), thus leading to the formation of aliphatic ketones. Isomerization of α-alkyltetrahydrofurans with ring opening at the C—O bond adjacent the alkyl group (the 1,2-bond) also takes place, but to a considerably lesser extent. Methyl-ethyl- and n-propyltetrahydrofurans isomerize in this manner to an extent not greater than 10% at a temperature not exceeding 250°. The resulting aldehydes readily undergo decarbonylation to the corresponding paraffinic hydrocarbons:



The experimental data obtained in the present investigation provide answers to the following four questions.

1. What is the effect of the length of the carbon chain of an alkyl radical in the α-position on the tendency of the tetrahydrofuran ring to isomerize by Reaction I or II. ?

2. What is the effect of temperature on the relative tendencies of the 1,2- and 1,5-bonds to undergo cleavage during isomerization of α-alkyltetrahydrofurans ?

3. How does isomerization proceed in the case of 2,5-dialkyltetrahydrofurans in which the alkyl radicals have different numbers of carbon atoms ?

4. In what manner do 2,2-dialkyltetrahydrofurans isomerize ?

The results of our experiments are presented in Table 1.

1) In order to obtain an answer to the first question, we investigated the isomerization of α-n-propyl-, α-n-butyl- and α-n-amyltetrahydrofurans under uniform conditions — in the vapor phase at 350°. The corresponding data of Table 1 show that an increase in the number of carbon atoms in the side chain of α-alkyltetrahydrofurans increases the tendency of the 1,2-C—O bond to undergo cleavage during isomerization of the ring, and, on the contrary, it decreases this tendency of the 1,5-C—O bond. α-n-Propyl-, α-n-butyl-, and α-n-amyltetrahydrofurans form, respectively, 76% 4-heptanone and 24% n-hexane, 67% 4-octane and 33% n-heptane, and 56% 4-nonanone and 44% n-octane. Thus, we have here a thoroughly specific dependence of the tendencies of the tetrahydrofuran ring to isomerize by Reactions I and II on the length of the alkyl side chain.

TABLE 1

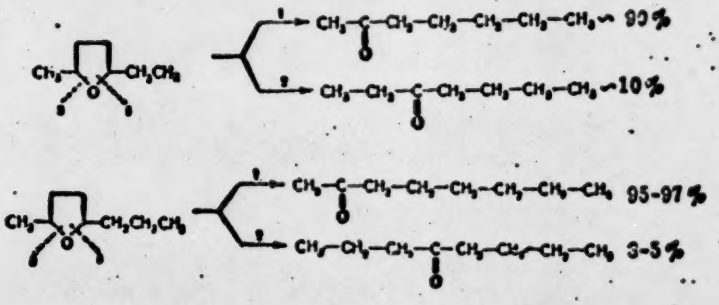
Products of the Isomerization of Tetrahydrofuran Homologs

Tetrahydrofuran homolog	Temp., deg C	Reaction products
α-n-Propyltetrahydrofuran	250	4-Heptanone (89%), n-hexane (11%)
α-n-Propyltetrahydrofuran	300	4-Heptanone (83%), n-hexane (17%)
α-n-Propyltetrahydrofuran	350	4-Heptanone (76%), n-hexane (24%)
α-n-Propyltetrahydrofuran	400	4-Heptanone (68%), n-hexane (32%)
α-n-Butyltetrahydrofuran	350	4-Octanone (67%), n-heptane (33%)
α-n-Amyltetrahydrofuran	350	4-Nonanone (56%), n-octane (44%)
2-Methyl-5-ethyltetrahydrofuran	300	2-Heptanone (~90%), 3-heptanone (~10%)
2-Methyl-5-propyltetrahydrofuran	300	2-Octanone (95-97%), 4-octanone (3-5%)
2-Methyl-2-ethyltetrahydrofuran	300	3-Methylpentane (~95-100%)
2-Methyl-2-n-propyltetrahydrofuran	300	3-Methylhexane (~95-100%)

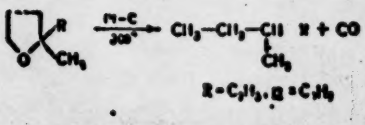
2) An answer to the second question posed above was obtained by an investigation of the isomerization of α-n-propyltetrahydrofuran at different temperatures: 250, 350, and 400°. The relative amounts of n-hexane and dipropyl ketone obtained from these reactions show that the course of the isomerization of the tetrahydrofuran ring is temperature dependent with regard to which bond, the 1,2- or the 1,5-C—O bond, is opened. Our experimental data, which are presented in Table 1, show that with an increase in temperature, there is an increase in the tendency of the tetrahydrofuran ring in α-alkyltetrahydrofurans to isomerize by ring cleavage at the C—O bond adjacent the alkyl radical. At 250, 300, 350, and 400°, the isomerization products of α-n-propyltetrahydrofuran contained, respectively, 11, 17, 24, and 32% n-hexane.

3) Since the nonequivalence of the 1,2- and 1,5-C—O bonds with respect to their tendency to undergo cleavage during isomerization of the substituted tetrahydrofuran ring depends on the length of the alkyl radical in the α-position, it might be expected that such nonequivalence would also appear in 2,5-dialkyltetrahydrofurans in which the alkyl groups contain different numbers of carbon atoms. Isomerization of 2-methyl-5-ethyltetrahydrofuran and 2-methyl-5-propyltetrahydrofuran did, in fact, proceed with opening of the ring occurring predominantly at that C—O bond which was adjacent the longest alkyl radical.

This "selectivity" was exhibited to the greatest extent by 2-methyl-5-n-propyltetrahydrofuran, and this is obviously in agreement with the data on the effect of the length of the alkyl radical in α-alkyltetrahydrofurans on the course of isomerization of the tetrahydrofuran ring:



4) Interesting peculiarities were discovered during the isomerization of those dialkyltetrahydrofurans in which both alkyl radicals are attached to the same α-carbon atom of the ring. Opening of the ring in this case proceeded exclusively at the C—O bond adjacent the alkyl side chains, which led, after decarbonylation of the intermediate aldehyde, to the formation of the corresponding aliphatic hydrocarbons:



It should be pointed out that isomerization of 2,2-dialkyltetrahydrofurans proceeds just as smoothly, but less readily than isomerization of α-alkyltetrahydrofurans.

EXPERIMENTAL PART

The α-alkyltetrahydrofurans and the 2,5-dialkyltetrahydrofurans were prepared by vapor-phase hydrogenation of the corresponding alkyl and dialkyltetrahydrofurans over palladium catalyst. The 2,2-dialkyltetrahydrofurans were synthesized by the method of Paul [2] from 2-methyl-4,5-dihydrofuran.

2-Methyl-5-n-propyltetrahydrofuran: b.p. 140-141.5° (755), d_4^{20} 0.8380; n_D^{20} 1.4200.

2-Methyl-2-ethyltetrahydrofuran: b.p. 120-121° (760), d_4^{20} 0.8561; n_D^{20} 1.4194.

2-Methyl-2-n-propyltetrahydrofuran: b.p. 143.5-144° (750), d_4^{20} 0.8528; n_D^{20} 1.4247.

The preparation of the catalyst and the conditions under which the experiments were carried out have been described in our previous paper [1]. The reaction products were separarated and purified by distillation in an efficient column. The properties of the ketones obtained in the isomerizations have been presented in reference [3]. 2-Heptanone and 3-heptanone, which were obtained during isomerization of 2-methyl-5-ethyltetrahydrofuran, boil close together; consequently, determination of the relative amounts formed was accomplished through preparation of the semicarbazones. Determination of the change in the melting point of the semicarbazone mixture with a change in the composition of the ketone mixture permitted determination of the relative amounts of 2-heptanone and 3-heptanone in the catalyzate.

After recrystallization from ethyl alcohol, semicarbazone mixtures had the following melting points (the 3-heptanone content in weight per cent is shown in parentheses): 120° (0), 113.5° (10), 106° (30), 92.5° (50), 84° (80), 96° (95), and 101° (100).

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SOME REGULARITIES IN THE FORMATION OF COMPOUNDS OF RHENIUM WITH TRANSITION METALS

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In a previous paper [1], the tendency of rhenium toward the formation in a number of binary systems of σ- and χ-phases was pointed out; these σ- and χ-phases possess the native crystal structure and occur widely in various binary and ternary systems of the transition metals. For this reason, rhenium binary systems are suitable objects for studying these compounds. χ-Phases are compounds with a structure of the type of α-Mn (body-centered cubic lattice with 58 atoms in the unit cell). A structure of the type of α-Mn is characterized by a distribution in conformity with the symmetry of the space group $I\bar{4}3m$, in particular, in the equivalent positions 2(a), 8(c), 24 (g), and 24 (g'), 10 of the positions [2(a) + 8(c)] corresponding to the greatest atomic volume [2]. In Table 1 are presented calculated data on the structure of α-Mn; these data show that positions (a) and (c) corresponding to average interatomic distances which are 5.4% greater than those of positions (g) and (g'). In conformity with this, a study of order in the χ-phase of the systems Mo – Cr – Fe, Ti – Cr – Co, and Ti – Cr – Re has shown that atomic components having the higher atomic radii are disposed in precisely these positions, (a) and (c) [3-5]. Moreover, the average compositions of the χ-phases can be expressed by formulas of the type $Mo_{10}Fe_{35}Cr_{13}$, $Re_{41}Ti_{13}$, and the like [3-6], from which it follows that the number of atoms of the component with the greater atomic radius (Table 2) is 10, i.e. the number of positions with the greater atomic volume.

For this, it may be assumed that in rhenium binary systems the tendency toward the formation of χ-phases is determined to a significant extent by a size factor. Values of the relative difference in atomic radii (the size factor) for transition metals in rhenium systems were calculated from the data of Table 2 using the formula:

$$P = \frac{R_{Me} - R_{Re}}{R_{Re}} 100\%.$$

The dependence of P on the number of the subgroup in the periodic systems of D. I. Mendeleev to which the element belongs is shown in the form of a graph (Figure 1), on which are noted those metals which, according to the literature [8-14], form compounds with rhenium. Consideration of this graph shows that a χ-phase is formed only with the metals of Subgroups IVA, VA and VIA, which have a positive size factor, i.e., a greater atomic radius than rhenium (Ti, Zr, Nb, Ta, Mo, and W). Metals from these groups of the periodic system with smaller atomic radii than rhenium (i.e., V and Cr) do not form χ-phases in binary systems. In those cases where the difference in atomic radii is small (about 2% for Mo and W), a χ-phase forms in the solid state by a peritectoid reaction [10, 12]. At the same time, in the case of elements (Ti and Zr) for which P = 5% and higher, a χ-phase separates from the liquid state by a peritectic reaction [11,13]. Obviously, this would be expected in the systems Re – Hf and Re – Ta, the equilibrium diagrams of which have not yet been studied. In ternary systems containing no rhenium and in which a χ-phase stable to the melting point is formed [3,5,6], the ratio of the atomic radii of the components also is in accordance with the rule stated above. For example, in the systems Mo – Cr – Fe, Ti – Co – Cr, and Ti – Cr – Fe, the Mo and Ti atoms have atomic radii which are 9.3%, 15.4%, and 15.9%, respectively, greater than the average of the atomic radii of the remaining two elements.

TABLE 1

Position	No. of neighboring atoms and their positions	Interatomic distance, A		Average interatomic distance, A
2 (a) X	4 A	2,82	2,74	2,75
	12 D_2	2,71		
8 (c) A	1 X	2,82	2,75	
	3 D_1	2,49		
	3 D_1	2,96		
	6 D_2	2,69		
	3 D_2	2,89		
24 (g) D_1	1 A	2,49	2,64	2,61
	1 A	2,96		
	6 D_1	2,67		
	1 D_2	2,45		
	2 D_2	2,51		
	2 D_2	2,66		
24 (g') D_2	1 X	2,71	2,57	
	1 A	2,89		
	2 A	2,69		
	1 D_1	2,45		
	2 D_1	2,51		
	2 D_1	2,66		
	1 D_2	2,24		
	2 D_2	2,38		

$$P = \frac{2,75-2,61}{2,61} \cdot 100 = 5,36\%$$

TABLE 2

Atomic Radii of the Transition Elements (in A) [7]

IV A	V A	VI A	VII A	VIII A	VIII B	VIII C
22 Ti	23, V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni
1,46	1,34	1,27	1,30	1,26	1,25	1,24
40 Zr	41 Nb	42 Mo	43(Tc)	44 Ru	45 Rh	46 Pd
1,60	1,45	1,39	1,36	1,34	1,34	1,37
72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt
1,59	1,45	1,40	1,37	1,35	1,35	1,38

However, it would not be correct to assume that the existence and stability of a χ-phase is wholly controlled by the size factor. One must also take into account the effect of the electron concentration in a manner similar to that which is well known in the case of σ-phases [2]. A connection with electron concentration is discerned first of all in the selection of the elements forming a χ-phase. One of the components (as in the case of σ-phase) must belong to Subgroup VII A or Group VIII, while the remaining components belong to Subgroup IV A, VA, or VI A. This provides for the χ-phase an electron concentration close to 6.5-7 electrons/atom. There has already been noted a rule [15] according to which the composition of a χ-phase corresponds to a higher electron concentration than does the composition of a σ-phase (when these compounds are formed in a single system).

In a number of transition metal systems, σ-phases exist together with χ-phases, and this permits establishment of a specific connection between these compounds. On the one hand, there is a similarity in the distribution of the atoms in the unit cell [3,16], and on the other hand, the compositions of the σ- and χ-phases obey the electron-concentration rule mentioned above. As may be seen from Figure 1, the existence of σ-phases in rhenium binary systems cannot be related solely to the size factor, since the formation of σ-phases occurs at values of P ranging from +17% (Re — Zr) to -8% (Re — Fe).

It can be stated, however, that when the size factor is close to 5%, i.e, when it is close to the value of the interatomic distances in α-Mn (Table 1), the tendency towards the formation of a σ-phase decreases and the tendency toward the formation of a χ-phase simultaneously increases. Thus, a σ-phase is not observed in the system Re — Ti [11], and the σ-phases in the systems Re—Nb and and Re — Ta are stable only from the melting point to t > 1200° C [9]. Consequently, the formation of a σ-phase is supressed under these conditions, since the structure of the χ-phase is preferred at this value of the size factor.

From the above, the following observations relative to the nature of χ-phases may be made. The formation of χ-phase in binary systems of rhenium with transition metals proceeds when the second component belongs to Subgroup IVA, VA, or VIA of the periodic system and possesses a greater atomic radius than rhenium. In this appears the dual nature of these phases as compounds whose existence and stability depend to an equal extent on the size factor and the electron-concentration rule. The conformity of the chemical composition of the χ-phase to a specific structural formula, which, in turn, is dependent on the dimensions of the component atoms, indicates the similarity to Laves phases. In addition, by some criteria χ-phases approach σ-phases, the existence of which is, to a great extent, connected with the electron concentration. Thus, χ-phases occupy an intermediate position between Laves and σ-phases.

However, distinctions between both of the latter phases and χ-phases should be pointed out. It is characteristic that χ-phases are significantly less widespread than Laves and σ-phases. According to the literature, only rhenium is capable of forming binary compounds with a structure of the type of α-Mn. This is indicative of the more vigorous conditions limiting the number of metallic systems in which compounds of this type can be formed. The exceptional tendency of rhenium toward the formation of χ-phases is probably attributable to the fact that this metal belongs to the same subgroup of the periodic system as manganese.

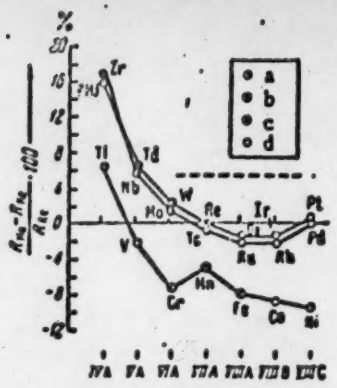

Fig. 1. Relation between the relative difference in atomic radii of elements and their tendency toward the formation of σ- and χ-phases in binary rhenium systems. a) a χ-phase is formed in the system; b) a σ-phase is formed in the system; c) both compounds are formed in the system; d) neither compound is formed in the system.

It is further known that the compositions of σ-phases crystallizing in binary and ternary systems differ depending on the positions of the components in the periodic system of D. I. Mendeleev. An accepted explanation of this is that σ-phases, like ordinary electron compounds, are characterized by a definite concentration of outer electrons and electronic vacancies. The composition of χ-phases corresponds approximately to a constant structural formula in all systems, which shows the lesser effect of electron concentration.

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SYNTHESIS OF SOME TRIETHYLSILOXYALKOXYTITANES

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Tetrakis[trialkyl(aryl)siloxy]titanes have been described in the literature [1-4]. Compounds which contain both trialkylsiloxy and alkoxy groups have not been studied.

As has been reported in the literature, the trialkyl(aryl)siloxy groups in tetrakis[trialkyl(aryl)siloxy]titanes are quite stable toward hydrolysis — incomparably more so than are alkoxy groups linked directly to the titanium. Therefore, it appeared to be of interest to study the properties of compounds containing both trialkylsiloxy and alkoxy groups.

In 1958, one of us described the synthesis of tris(trimethylsiloxy)butoxytitane by esterification of tris(trimethylsiloxy)titanium chloride with butyl alcohol [1]; this is the sole known member of this class of compounds. However, owing to the difficulty of obtaining trialkylsiloxytitanium chlorides, this method is not very practicable. Therefore, the possibility of synthesizing triethylsiloxytitanes by the direct interaction of triethylsilanol with butyl orthotitanate and propyl orthotitanate was studied in the present investigation.

In spite of the report in the literature [3] that the reaction between butyl orthotitanate and triphenylsilanol proceeds with complete replacement of all butoxy groups by triphenylsiloxy groups, we were able to show that when triethylsilanol is reacted with butyl orthotitanate and propyl orthotitanate in the presence of metallic sodium as a catalyst, transesterification proceeds with the formation not only of tetrakis(triethylsiloxy)titane, but also of products of varying degrees of substitution depending on the ratio of the reacting components.

The interaction of butyl orthotitanate and of propyl orthotitanate proceeds according to the equations

$$Ti(OR)_4 + n\,(C_2H_5)_3SiOH \xrightarrow{Na} [(C_2H_5)_3SiO]_n\,Ti(OR)_{4-n} + n\,ROH,$$

where R is C_3H_7 or C_4H_9, and n is 1, 2, 3, or 4.

In the course of the study of this reaction, we obtained tris(triethylsiloxy)butoxytitane in a yield of 46% of theoretical, bis(triethylsiloxy)dibutoxytitane (34%), and bis(triethylsiloxy)dipropoxytitane (21%). The physical constants, yields, and analytical data for these triethylsiloxyalkoxytitanes are presented in Table 1. The stability of these compounds toward hydrolysis was studied.

EXPERIMENTAL PART

1. Synthesis of bis(triethylsiloxy)dibutoxytitane. 105.6 g (0.8 mole) of triethylsilanol with a b.p. of 70°/18mm, n_D^{20} 1.4338; 136 g (0.4 mole) of butyl orthotitanate, b.p. 165-167°/4 mm, n_D^{20} 1.4924, and 0.02 g of sodium were placed in a flask fitted with a Vigreux column. The mixture was slowly heated, the temperature of the overhead vapors being maintained below 118°. 54.2 g (91.7%) of butyl alcohol distilled within the temperature range of 118-120°. The remaining material was fractionated under vacuum, and 61.2 g (34%) of bis(triethylsiloxy)dibutoxytitane was obtained; b.p. 182°/4 mm, d_4^{20} 0.9517; n_D^{20} 1.4758.

2. Synthesis of tris(triethylsiloxy)butoxytitane. The reaction between 68 g (0.2 mole) of butyl orthotitanate and 79.2 g (0.6 mole) of triethylsilanol in the presence of 0.015 g of sodium was carried out similarly to the preceding reaction. 39.9 g (90%) of butyl alcohol distilled at a temperature of 117-119°. The remaining material

TABLE 1

Substance	B.p., deg C (mm Hg)	n_D^{20}	d_4^{20}	MR found	MR calc.	Yield, %	Found, % C	Found, % H	Found, % Si	Found, % Ti	Calculated, % C	Calculated, % H	Calculated, % Si	Calculated, % Ti
I	182° (4)	1,4758	0,9517	135,69	133,96	34	53,24	10,65	13,25	10,27	52,63	10,52	12,28	10,52
II	174—177 (3)	1,4687	0,9378	152,65	151,93	46	51,79	10,49	17,23	9,49	51,37	10,50	16,34	9,33
III	14[illegible]—146 (1,5)	1,4800	0,9680	125,60	124,63	21	50,10	10,72	12,43	11,24	50,46	10,28	13,08	11,21

Note. I = $[(C_2H_5)_3SiO]_2Ti(OC_4H_9)_2$; II = $[(C_2H_5)_3SiO]_3TiOC_4H_9$; III = $[(C_2H_5)_3SiO]_2Ti(OC_3H_7)_2$.

was distilled under vacuum, and 47.3 g (40%) of tris(triethylsiloxy)butoxytitane was obtained; b.p. 174–177°/3 mm d_4^{20} 0.9378; n_D^{20} 1.4687.

3. Synthesis of bis(triethylsiloxy)dipropoxytitane. A mixture of 113.6 g (0.4 mole) of propyl orthotitanate 105.6 g (0.8 mole) of triethylsilanol, and 0.02 g of sodium was gradually heated, the temperature being kept below 90°. 45.7 g (95%) of propyl alcohol distilled. The remaining material was distilled under vacuum, and 36.1 g (21.0%) of bis(triethylsiloxy)dipropoxytitane was obtained; b.p. 144–146°/1.5 mm; d_4^{20} 0.9680; n_D^{20} 1.4800.

All of the syntheses were carried out under conditions such that atmospheric moisture was excluded.

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THE STANDARD HEAT OF FORMATION OF BORON OXIDE

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(Presented by Academician V. N. Kondrat'ev, April 4, 1959)

The standard heat of formation of B_2O_3 is a fundamental value in the thermochemistry of boron compounds. Its determination is attended by considerable experimental difficulties, as a consequence of which the values in the literature [1-13] are not in good agreement (ranging between extremes of 270 to 368 kcal /mole). The selection of a reliable value is not possible, since in part of the work [1-9] it is impossible to evaluate the errors due to side reactions, and in the other part [10-13] there is no information permitting an evaluation of the results.

The present paper reports an experimental determination of this value by three independent routes, which led to the same result (within the limits of error of the measurements).

The calorimetric determinations employed two samples of amorphous boron containing only traces of the crystalline modification. After the removal of adsorbed gases, the following impurities were found in Sample 1: O, 0.23%; H, 0.12%; N, 0.005%; and total Ca, Mg, and Cu, about 0.01%; Sample 2, which was prepared in the same manner as Sample 1, contained 99.3% ± 0.4% boron and was "spectroscopically pure".

EXPERIMENTAL PART

1. Combustion of boron in oxygen. The combustion was carried out without the addition of a subsidiary readily combustible material in order to avoid error due to its incomplete combustion in the presence of boron, to its possible interaction with boron at high temperatures, and to the uncontrolled hydration of B_2O_3. The experiments were carried out as follows: a weighed sample of 0.17-0.25 g of boron (Sample 2) in a quartz crucible was heated in the bomb calorimeter for about 3 minutes at 1000° under an oxygen pressure of 7 atm; a small electric heater was employed for this purpose. 35-40% of the boron burned. The amount of boron oxide formed was calculated from the results of the weighings of the crucible containing the material before and after the experiment* (under conditions which excluded hydration) and from the determination of the small amount of oxide (0.3-1.7%) which vaporized during the experiment (the boron oxide deposit on the internal parts of the bomb was dissolved in water, and the solution was titrated with base in the presence of mannitol).

Analysis of the experimental data established that only one oxide — B_2O_3 — was obtained by the combustion of the boron and that the error due to combustion of any hydrogen contained in the boron could be neglected. Five determinations established:

$$\Delta H_f^\circ \quad B_2O_{3(glass)} = -293.7 \pm 1.3 \text{ kcal/mole}$$

Here and in the remainder of the text, the value ΔH°_f refers to $\vartheta = 25°$ and $P = 1$ atm; 1 calorie was taken as 4.1840 absolute joules; the crystalline state was taken as the standard state for boron; for the conversion $B_{amor.} = B_{cryst.}$, $\Delta H = -0.4$ kcal / mole [14]. The error in the results is expressed as the root mean square error.

* The determination of boron oxide by treatment of the reaction mass with water and subsequent titration of the boric acid is unreliable owing to the difficulty in completely extracting all of the oxide.

2. Direct determination of the heat of formation of boron nitride* and calculation of ΔH^0_f of B_2O_3 using the reliably established value for the heat of combustion of boron nitride [18]. The reaction between boron and nitrogen is suitable for calorimetry, since it is not accompanied by side reactions — only one boron nitride, BN, is known; small amounts of O, H, and N in the boron samples do not interfere with the determination; and boron nitride is not hygroscopic.

The reaction was carried out in a bomb calorimeter, fitted with an electric heater, under 10 atm of nitrogen free of oxygen and ater. A weighed sample of 0.2 g of boron (Sample 1) was heated in the quartz crucible at 1300° for about 3 minutes. Under these conditions, about 40% of the boron was converted to the nitride. The amount of boron nitride formed was calculated from the results of weighings of the crucible containing the substance before and after the experiment. X-ray investigation of the reaction product established the presence of only one crystal structure, — the hexagonal modification of BN.

The following value was obtained from eight determinations:

$$\Delta H_f \quad BN = -60{,}7 \pm 0{,}3 \text{ kcal/mole}$$

Combining this result with $\Delta H = -90.2$ kcal /mole for the combustion of boron nitride [18], we have:

$$\Delta H^0_f \quad B_2O_{3(glass)} = -301{,}8 \pm 1{,}4 \text{ kcal/mole}$$

3. Direct determination of the heat of formation of BCl_3 and calculation of ΔH^0_f of B_2O_3 using reliable values for the heat of hydrolysis of BCl_3 [19], the heat of solution of B_2O_3 [20], the heat of formation of H_2O and of a solution of HCl of the appropriate concentration [14].

Only BCl_3 is obtained from the interaction of boron and chlorine, and the BCl_3 does not form compounds with hydrogen chloride [21], which is always present as an impurity in the chlorine. The experiments were carried out as follows: a weighed sample of 0.01-0.2 g of boron (Sample 1) in the quartz crucible was heated in the bomb calorimeter by means of the electric heater for 7-10 minutes at 450-500° under 6 atm of carefully dried chlorine. After the removal of the gases from the bomb, the amount of unreacted boron, which usually comprised 0.2-0.3% of the original amount of boron, was determined by weighing the quartz crucible. The measured heat effect was adjusted by the introduction of a small correction (1 calorie) for hydrolysis of the BCl_3 during the experiment. Depending on the initial amount of boron, after the reaction the bomb contained only $BCl_{3,g}$ or a mixture of $BCl_{3,l}$ with a constant amount of $BCl_{3,g}$ (bomb volume was 260 cc). From the results of the experiments, we found (after 7 determinations, a; after 5 determinations, b):

$$\text{a} \quad \Delta H^0_f \quad BCl_{3,l} = -102{,}9 \pm 0{,}6 \text{ kcal/mole}$$
$$\text{b} \quad \Delta H^0_f \quad BCl_{3,g} = -97{,}0 \pm 0{,}7 \text{ kcal/mole}$$

Using ΔH^0_f BCl_{3l} and carrying out the calculation indicated above, we have:

$$\Delta H^0_f \quad B_2O_{3(glass)} = -301{,}6 \pm 1{,}2 \text{ kcal/mole}$$

A liquid calorimeter with an isothermal jacket was used in all three routes. The temperature rise was measured with an calorimetric mercury thermometer with an accuracy of $\pm 2 \cdot 10^{-4}$ degrees. The bomb heater was constructed from calcium monoaluminate (first method) or from alundum and clay (second method); the heating element was platinum. The quartz crucible or cell which contained the substance under investigation was protected from reaction with the furnace material by means of a platinum jacket. In the third route, the heater was constructed from Pyrex glass in the form of a small Dewar vessel, between the walls of which was placed a constantan heating element; the bomb was coated with silver covered with AgCl and had a nickel cover. In the first route, the electrical energy used by the heater was determined by the method described by Neumann, Kröger and Haebler [22] (an empirical calibration equation); in the second route, the electrical energy was determined by means of a specially developed apparatus, the basic elements of which are alternating current of high accuracy**. The usual

* The literature values of ΔH^0_f of BN were obtained by indirect routes [4,15-17], and are not reliable.

** A description of the apparatus will be published in the Journal of Physical Chemistry.

potentiometric was used in the third route. The calorimeter constant was determined in the first two cases by determination of the heat of combustion of a benzoic acid standard, and in the third case by an electrical method using the bomb heater.

The values of ΔH^0_f of B_2O_2 obtained in the present work by three independent methods are in good agreement, within the limits of experimental error, which indicates the absence of substantial systematic errors in each of the determinations.

The weighted averages of the three results is:

$$\Delta H^0_f \quad B_2O_{3(glass)} = -301.1 \pm 0.8 \text{ kcal/mole (from } B_{cryst.} \text{ and } O_{2,g}).$$

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SEVEN-COMPONENT RECIPROCAL SYSTEM OF 16 SALTS, Li, Na, Rb, Tl ‖ Br, Cl, NO_3, SO_4, IN MELTS

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(Presented by Academician I. I. Chernyaev, April 4, 1959)

The investigation of multicomponent systems has a great significance in the study of natural and technological processes (thermal and thermochemical treatment of metals, heat carriers, electrochemical production of light metals from molten media, nonferrous metallurgy, etc.).

A complete study of multicomponent systems requires the expenditure of a large amount of labor. Routes for a simpler solution of questions relating to reaction in multicomponent systems were pointed out in the thirties by N. S. Kurnakov in his papers on triangulation and on singular stars* in chemical equilibrium diagrams and in the papers of his co-workers [1-4].

The composition of multicomponent systems is represented geometrically by means of n-dimensional polytopes.

The following component systems** enter into the composition of the seven-component system studied in the the present work, Li, Na, Rb, Tl ‖ Br, Cl, NO_3, SO_4 :

16 single-component systems of the type AX
48 binary systems of the type AX — BX
32 ternary systems of the type A ‖ X, Y, Z
36 ternary reciprocal systems of the type A, B ‖ X, Y
8 quaternary systems of the type A ‖ X, Y, Z, T
48 quaternary reciprocal systems of the type A, B ‖ X, Y, Z
12 quinary reciprocal systems of 8 salts A, B ‖ X, Y, Z, T
16 quinary reciprocal systems of 9 salts A, B, C ‖ X, Y, Z
8 six-component systems of 12 salts A, B, C ‖ X, Y, Z, T

Finding a singular star. A singular (equilibrium) star is determined by the stable diagonals of ternary reciprocal systems, by the stable diagonal triangles of quaternary reciprocal systems, by the stable diagonal tetrahedrons of quinary reciprocal systems, etc. [2,3,4].

In practice, it is satisfactory to use tables of the indices of the vertexes of the polytopes used for the geometrical representation of the compositions of multicomponent systems ; the vertex indices are determined by the number of stable diagonals passing through a given polytope vertex.

In Table 1 are presented vertex indices for reciprocal systems from six, eight, nine, and twelve salts.

The composition diagram for the quaternary reciprocal system of 6 salts is a prism [6, 8] which is divided by two stable diagonal triangles, having in common the most stable rib (of a singular star), into three stable cells — tetrahedrons.

The axis of the singular star is defined by the indexes 2-2 (here and in the remainder of the article, the

* For a description of "singular stars", see Chem. Abs. 30, 5861[1] (1936)—Trans.

** A, B, and C are cations; X, Y, and Z are anions.

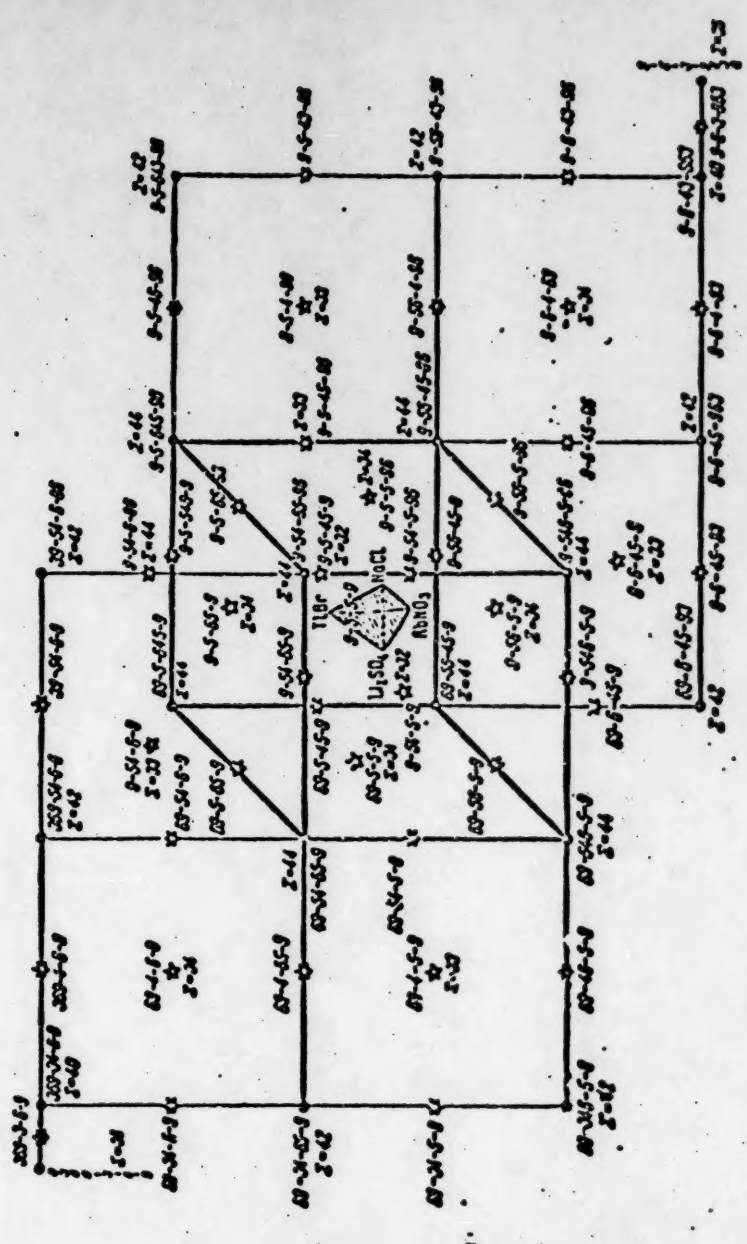

Fig. 1. Singular star of the reciprocal system of 16 salts: Li, Na, Rb, Tl ‖ Br, Cl, NO_3, SO_4.

numbers of the first line are separated from the numbers of the succeeding lines by a hyphen); the intersecting triangles are: 1) 2-21; 2) 12-2.

The composition diagram of the quinary reciprocal system of 8 salts is a four-dimensional prism of the first type [5] divided by three diagonal tetrahedrons with a common rib (axis of the singular star) into four stable cells — pentatopes. The axis of the singular star is defined by the indices 3-3; the dividing tetrahedrons are: 1) 3-321, 2) 123-3, 3) 32-23. For the quinary reciprocal system of 9 salts, the composition diagram is a four-dimensional prism of the second type [2,6,7]. There are five possible types of division of the prism, A, B, C, D, and E. The indices for type A are presented in the Table. Moreover, the four-dimensional prism of the second type is divided by six tetrahedrons, of which four have a common triangular base — the most stable "basal" triangle, which is defined by the indices $4\text{-}3\text{-}3^b$; the dividing tetrahedrons are: 1) $24\text{-}3\text{-}3^2$, 2) $4\text{-}2\text{-}3^23^b$, 3) $24\text{-}3\text{-}3^b$, 4) $4\text{-}31\text{-}3^b$, 5) $4\text{-}32\text{-}3^b$, 6) $4\text{-}3\text{-}3^23^b$; the stable cells are 6 pentatopes.

TABLE 1

Vertex Indexes of the Reciprocal System

Cations	Anions X	Y	Z	T	Σ
Reciprocal system of 6 salts A, B ‖ X, Y, Z					
A	0	1	2	--	3
B	2	1	0	—	3
Σ	2	2	2	-	6
Reciprocal system of 8 salts A, B ‖ X, Y, Z, T					
A	0	1	2	3	6
B	3	2	1	0	6
Σ	3	3	3	3	12

Cations	Anions X	Y	Z	T	Σ
Reciprocal system of 9 salts A, B, C ‖ X, Y, Z. Type A					
A	0	2	4	—	6
B	3	1	2	—	6
C	3[a]	3[b]	0	—	6
Σ	6	6	6	—	18
Reciprocal system of 12 salts A, B, C ‖ X, Y, Z, T: Type 4 C					
A	0	2	4	6	12
B	3[a]	3[b]	3[c]	3[d]	12
C	6	4	2	0	12
Σ	9	9	9	9	36

TABLE 2

Cations	Anions Br	Cl	NO_3	SO_4	Σ
Li	0	3	3	9	18
Na	3	5	4	6	18
Rb	6	4	5	3	18
Tl	9	6	3	0	18
Σ	18	18	15	18	72

In the six-component reciprocal system of 12 salts, the composition diagram is a five-dimensional prism of the second type [4]. The indices for Type 4C* are presented in the table; the singular star consists of three rings containing 10 stable cells — hexatopes — divided by 12 pentatopes. Three tetrahedra, which are "basal" for each ring, have in common the most stable rib. The stable elements are defined by the following indices: rib, 6-6; basal tetrahedrons: 1) $46\text{-}3^{c}\text{-}6$, 2) $6\text{-}3^{b}3^{c}\text{-}6$, 3) $6\text{-}3^{c}\text{-}46$.

Reciprocal system of 16 salts, Li, Na, Rb, Tl ‖ Br, Cl, NO_3, SO_4.

The composition diagram of the seven-component reciprocal system of 16 salts, Li, Na, Rb, Tl ‖ Br, Cl, NO_3, SO_4, is a six-dimensional polytope [4]. The vertex indices for this polytope are presented in Table 2. The singular star contains the most stable "basal" tetrahedron 9-5-5-9, Li_2SO_4-NaCl - $RbNO_3$-TlBr (first reported by V. P. Radishchev), which is found in the center of the cube and is common to all six pentatopes in the centers of the cube faces; 12 basal pentatopes are located in the center of the square rings; 30 hexatopes are disposed at the center of the rib; 20 pentatopes are located at the vertex of squares and two extensions.

Similar tables of indices defining the number of unstable diagonals of ternary reciprocal systems, the diagonals passing through the vertexes of polytopes, permitted us to find the nonequilibrium tetrahedron in the system of 16 salts. It was formed by the salts LiBr-Tl_2SO_4-RbCl-$NaNO_3$, which actively interact forming, as reaction products, salts which lie at the vertexes of a stable tetrahedron. Both tetrahedrons are disposed in the six-dimensional space of the diagram in a manner such that they intersect each other along the conversion line according to the equation:

$$LiBr + NaNO_3 + RbCl + \frac{1}{2}Tl_2SO_4 = \frac{1}{2}Li_2SO_4 + NaCl + RbNO_3 + TlBr.$$

The singular star of the system of 16 salts is presented in Figure 1. Attention is directed to the presence in the star of a twofold symmetry with a center of symmetry.

The indices of all symmetrical elements of the diagram are equal in absolute value and in the sum of the indices of the reciprocal pairs; the edge pentatopes in the extensions 0369-3-6-9 and 9-6-3-9630 and at the vertexes of the cube are opposed along the diagonals 69-5-645-9 and 9-546-569, etc. The observed symmetry considerably facilitates the construction of the singular star.

On the basis of an experimental determination of the melting curve of the system Li_2SO_4-NaCl-$RbNO_3$-TlBr, it was established that the reciprocal system Li, Na, Rb, Tl ‖ Br, Cl, NO_3, SO_4 can be assigned to the class of reversible reciprocal systems.

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ESTERS OF ORGANIC THIO ACIDS OF BORON AND SOME OF THEIR REACTIONS

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Esters of dialkylthioborinic acids, which have been obtained by one of us and Yu. N. Bubnov by the action of sulfur [1] or mercaptan [2] on trialkylborines, are very reactive compounds, useful for the synthesis of various organic compounds of boron. In this connection, it appeared to be of considerable interest to prepare esters of alkylthioboronic, arylthioboronic, and diarylthioborinic acids and to study their behavior with respect to different reagents.

The only known esters of aliphatic thioboronic acids are the dimethyl ester of methylthioboronic acid, prepared by the interaction of trimethyl thioborate and the methyl ester of dimethylthioborinic acid [3], the didodecyl ester of β-chlorovinylthioboronic acid, synthesized by the action of dodecyl mercaptan on the dimethyl ester of β-chlorovinylboronic acid, and the octyl ester of β-chlorovinylchloroborinic acid [ClCHCHB(Cl)SC_8H_{17}], prepared by the action of octyl mercaptan on β-chlorovinylboronyl dichloride [4]. Of the esters of aromatic-substituted thio acids of boron, only the di-n-amyl ester of phenylthioboronic acid has been described; this compound was obtained by the interaction of phenyldichloroborine and sodium n-amyl mercaptide [5].

We found [1] that di-n-butyl esters of alkylthioboronic acids are obtained in good yields by refluxing alkyldichloroborines and alkyldibromoborines with n-butyl mercaptans:

$$RBX_2 + 2n\text{-}C_4H_9SH = RB(SC_4H_9\text{-}n)_2 + 2HX$$
(I)

$R = n\text{-}C_3H_7$, $n\text{-}C_4H_9$, $iso\text{-}C_5H_{11}$; $X = Cl$, Br.

The di-n-butyl ester of phenylthioboronic acid (II) was obtained by the same method from phenyldichloroborine:

$$C_6H_5BCl_2 + 2\,n\text{-}C_4H_9SH = C_6H_5B(SC_4H_9\text{-}n)_2 + 2HCl$$
(II)

Diphenylchloroborine and di-α-naphthylchloroborine react analogously with n-butyl mercaptan, forming the corresponding n-butyl esters of diphenylthioborinic acid (III, Ar = C_6H_5) and di-α-naphthylthioborinic acid (III, Ar = α-$C_{10}H_7$).

$$Ar_2BCl + n\text{-}C_4H_9SH = Ar_2BSC_4H_9\text{-}n + HCl \quad Ar = C_6H_5,\ \alpha\text{-}C_{10}H_7.$$
(III)

All of these organic thio acids of boron are highly reactive, which permits their conversion to other, diverse classes of organic boron compounds. Diesters of alkylthioboronic acids are smoothly converted by the action of

ethylenediamine to cyclic compounds—2-alkyl-2-boro-1,3-diazolidines (IV) [2-alkyl-1,3,2-diazoborolidine]—accompanied by the liberation of n-butyl mercaptan:

$$RB(SC_4H_9\text{-}n)_2 + NH_2(CH_2)_2NH_2 = RB\begin{matrix}NH-CH_2\\ |\\ NH-CH_2\end{matrix} + 2n\text{-}C_4H_9SH$$

$R = n\text{-}C_3H_7,\ iso\text{-}C_5H_{11}$ (IV)

This route was used to synthesize 2-propyl-2-boro-1,3-diazolidine (IV, R = n-C_3H_7) and 2-isoamyl-2-boro-1, 3-diazolidine (IV, R = iso-C_5H_{11}) which are liquid materials. The methyl derivative of 2-borodiazolidine (m.p. 43°) was prepared by Goubeau and Zappel [6] by heating trimethylborine with ethylenediamine at 440°.

It should also be mentioned that 2-isoamyl-2-borodiazolidine is obtained by the action of ethylenediamine on isoamyldichloroborine; however, we were unable to prepare the n-propyl derivative of 2-borodiazolidine by this method.

Esters of alkyl- and arylthioboronic acids are converted by the action of ammonia in the cold into the corresponding B-trialkyl- or B-triarylborazoles (V). From the di-n-butyl ester of isoamylthioboronic acid was obtained B-triisoamylborazole (V, R = iso-C_5H_{11}) in 88% yield, previously prepared by us by the action of ammonia on isoamyldichloroborine [7] with a yield of 49%; B-triphenylborazole (V, R = C_6H_5) was readily formed by the action of ammonia on the ester of phenylthioboronic acid.

$$3RB(SC_4H_9\text{-}n)_2 + 3NH_3 = (BBNH)_3 + 6\,n\text{-}C_4H_9SH \quad R = iso\text{-}C_5H_{11},\ C_6H_5. \quad (V)$$

The reaction between the ester of phenylthioboronic acid and diethylamine proceeded in only one direction with the formation of phenylbis (diethylamino) borine (VI) in 80% yield, while the amino compound was obtained in only 14% yield from phenyldichloroborine [8].

$$C_6H_5B(SC_4H_9\text{-}n)_2 + 2(C_2H_5)_2NH = C_6H_5B[N(C_2H_5)_2]_2 + 2n\text{-}C_4H_9SH. \quad (VI)$$

The n-butyl ester of diphenylthioborinic acid was converted by the action of n-butylamine to diphenylbutylaminoborine (VII) in 80% yield

$$(C_6H_5)_2BSC_4H_9\text{-}n + n\text{-}C_4H_9NH_2 = (C_6H_5)_2BNHC_4H_9\text{-}iso + n\text{-}C_4H_9SH \quad (VII)$$

Esters of diphenylthioborinic and di-α-naphthylthioborinic acids react with ammonia in the cold, forming respectively, diphenylaminoborine (VIII, Ar = C_6H_5) and di-α-naphthylaminoborine (VIII, Ar = α-$C_{10}H_7$) in good yields

$$Ar_2BSC_4H_9\text{-}n + NH_3 = Ar_2BNH_2 + n\text{-}C_4H_9SH \qquad Ar = C_6H_5,\ \alpha\text{-}C_{10}H_7.$$
(VIII)

EXPERIMENTAL PART

All operations were carried out in a nitrogen atmosphere.

Di-n-butyl ester of n-propylthioboronic acid (I), R = n-C_3H_7. To 20.5 g (0.096 mole) of n-propyldibromoborine, prepared by the action of boron tribromide on n-propylboronic anhydride, was added 23 g (0.25 mole) of n-butyl mercaptan. The reaction was exothermic. Upon completion of the addition of the n-butyl mercaptan, the reaction mixture was refluxed for 13 hours. The excess n-butyl mercaptan was distilled, and distillation of the residue under vacuum gave 22.4 g (90 %) of a material with a b.p. of 149-150° at 13 mm, d_4^{20} 0.9106; n_D^{20} 1.4956.

Found %: C 56; 56.83; 83*; H 10.92; 10.80 $C_{11}H_{25}BS_2$. Calculated %: C 56.88; H 10.85.

Di-n-butyl ester of n-butylthioboronic acid (I), R = n-C_4H_9. In a similar manner but with a refluxing time of 15 hours, from 21.7 g (0.095 mole) of n-butyldibromoborine, prepared by the action of boron tribromide on n-butylboronic anhydride, and 25 g (0.28 mole) of n-butyl mercaptan was obtained 20.7 g (88.5%) of the di-n-butyl ester of n-butylthioboronic acid, b.p. 148-150° at 7 mm, d_4^{20} 0.9045; n_D^{20} 1.4936.

* As in original-Publisher.

Found %: C 58.38; 58.71 ; H 11.02; 11.09 $C_{12}H_{27}BS_2$. Calculated %: C 58.51; H 11.05.

Di-n-butyl ester of isoamylthioboronic acid (I), R = C_5H_{11}. Upon refluxing for 13 hours 22.5 g (0.147 mole) of isoamyldichloroborine [7] and 38 g (0.42 mole) of n-butyl mercaptan, there was obtained 30.6 g (80%) of a substance with a b.p. of 153.5-154° at 6 mm, d_4^{20} 0.8988; n_D^{20} 1.4871.

Found %: C 60.13; 60.20; H 11.27; 11.24 $C_{13}H_{29}BS_2$. Calculated %: 59.98; H 11.23.

Di-n-butyl ester of phenyl thioboronic acid (II). A mixture of 28.3 g (0.178 mole) of phenyldichloroborine and 33 g (0.369 mole) of n-butyl mercaptan was refluxed for 7 hours. The unreacted butyl mercaptan was distilled, and the residue was fractionated. There was obtained 25.1 g (53 %) of the di-n-butyl ester of phenylthioboronic acid, b.p. 137.5-138.5° at 1.5 mm, d_4^{20} 0.9865, n_D^{20} 1.5464.

Found%: C 62.18; H 8.89; B 4.42 $C_{14}H_{23}BS_2$. Calculated %: C 63.15; H 8.74; B 4.08.

n-Butyl ester of diphenylthioborinic acid (III). Ar = C_6H_5. A mixture of 10 g (0.05 mole) of diphenylchloroborine [11] and 4.5 g (0.05 mole) of n-butyl mercaptan was heated at 100-120° for 3 hours. The reaction mixture was distilled, and 8.4 g (69%) of the n-butyl ester of diphenylthioborinic acid was obtained; b.p. 178-180° at 7 mm d_4^{20} 1.001; n_D^{20} 1.5871.

Found %: C 74.48; 74.58; H 7.74; 7.66; B 4.35; 4.20; S 12.41; 12.57 $C_{16}H_{19}BS$. Calculated %: C 75.59; H 7.53; B 4.25; S 12.61.

n-Butyl ester of di-α-naphthylthioborinic acid (III). Ar = α-$C_{10}H_7$. 6.5 g (0.07 mole) of n-butyl mercaptan was added to 21.6 g (0.07 mole) of di-α-naphthylchloroborine [11] dissolved in 15 ml of benzene. Reaction took place at room temperature. After an hour, the solution was heated at the boiling point for 1 hour. The solution was then distilled, and 20.3 g (80 %) of the n-butyl ester of di-α-naphthylthioborinic acid was obtained; the compound, a light-yellow viscous oil, had a b.p. of 245-247°, at 2 mm.

Found %: C 81.56; 81.59; H 6.62; 6.63; B 3.37; S 8.17 $C_{24}H_{23}BS$. Calculated %: C 81.35; H 6.54; B 3.05 S 9.05.

2-Isoamyl-2-boro-1,3-diazolidine [2-isoamyl-1,3,2-diazoborolidine] (IV), R = iso-C_5H_{11}. 1) To ice-cooled dibutyl ester of isoamylboronic acid (11.6 g, 0.044 mole) was added 2.68 g (0.044 mole) of ethylene diamine; evolution of heat was observed. The reaction mixture was then refluxed for 2 hours (bath temperature, 150°). After distillation of the n-butyl mercaptan (7.2 g or 90%), the residue was distilled under vacuum. There was obtained 5.5 g (85.5%) of 2-isoamyl-2-boro-1,3-diazolidine in the form of a colorless, viscous liquid with a b.p. of 80-81° at 12 mm. d_4^{20} 0.9165; n_D^{20} 1.4872.

Found %: C 60.07; 60.30; H 12.49; 12.40; B 8.04; 8.04 $C_7H_{17}BN_2$. Calculated %: C 60.03; H 12.24; B 7.72.

Molecular weight: 146; calculated, 140.

2) 14 g (0.09 mole) of isoamyldichloroborine was dissolved, with cooling, in 60 ml of ether, and to the solution, at -25°, was added 11 g (0.18 mole) of ethylenediamine in 20 ml of ether. The reaction mixture was stirred at room temperature for 2 hours, and the precipitated ethylenediamine hydrochloride was filtered and extracted with boiling ether. After distillation of the solvent, the residue was distilled. There was obtained 9.9 g (77.4%) of 2-isoamyl-2-boro-1,3-diazolidine with a b.p. of 80-81° at 12 mm.

2-n-Propyl-2-boro-1,3-diazolidine (IV), R = n-C_3H_7. A mixture of 14.09 g (0.064 mole) of the dibutyl ester of n-propyl boronic acid and 3.85 g (0.064 mole) of ethylenediamine was heated at 140-150° for 2 hours. There was obtained 6 g (83.6%) of 2-n-propyl-2-boro-1,3-diazolidine with a b.p. of 67-68° at 25 mm. d_4^{20} 0.9406, n_D^{20} 1.4941.

Found%: C 53.43; 53.83; H 11.86; 11.84; B 9.59; 9.41 $C_5H_{13}BN_2$. Calculated %: C 53.62; H 11.69; B 9.66.

B-Triisoamylborazole (V), R = iso-C_5H_{11}. A stream of dry ammonia was passed for 40 minutes into the dibutyl ester of isoamylthioboronic acid (10.3 g) at room temperature. The temperature of the reaction mixture rose to 40-50° due to the exothermic heat. After distillation under vacuum of the n-butyl mercaptan (6 g, 84.5%), distillation of the residue gave 3.35 g (87.7%) of B-triisoamylborazole [7] with a b.p. of 114-115.5° at 0.1 mm.

B-Triphenylborazole (V), R = C_6H_5. A stream of ammonia was passed for 15 minutes into a solution of 4.2 g of n-butyl ester of phenylthioboronic acid in 6 ml of benzene. The benzene and n-butyl mercaptan were distilled under vacuum, and the resulting crystalline precipitate was washed with isopentane. There was obtained 1.5 g (95%) of B-triphenylborazole, which, after recrystallization from a mixture of benzene and isopentane, had an m.p. of 178-180° (in sealed capillary) [8].

Phenylbis (diethylamino) borine (VI). A mixture of 9.9 g (0.037 mole) of the di-n-butyl ester of phenylthioboronic acid and 6.1 g (0.084 mole) of diethylamine was heated at 90-95° for 5 hours. The unreacted diethylamine and the butylamine formed during the reaction were distilled under a slight vacuum, and the residue was fractionally distilled. There was obtained 6.9 g (80%) of phenylbis(diethylamino)borine with a b.p. of 113-117° at 2.5 mm. After a second distillation, the substance had a b.p. of 115.5-116.5° at 2.5 mm, d_4^{20} 0.9406, n_D^{25} 1.5183.

Diphenylisobutylaminoborine (VII). A mixture of 6.9 g (0.027 mole) of the n-butyl ester of diphenylthioborinic acid and 2 g (0.027 mole) of n-butylamine was heated at the boiling point for an hour. Distillation gave 5.25 g (80.7%) of diphenylisobutylaminoborine with a b.p. of 161-163° at 3 mm, n_D^{20} 1.560.

Diphenylaminoborine (VIII), Ar = C_6H_5. A stream of dry ammonia was passed for 1 hour into a benzene solution of 3.3 g of the n-butyl ester of diphenylthioborinic acid at room temperature. A slight evolution of heat was observed, and a colorless crystalline precipitate formed. There was obtained 2 g (85.4%) of diphenylaminoborine with an m.p. of 141-142° (sealed capillary).

Found %: C 79.15; 79.36; H 6.66; 6.61; B 5.95; 5.79; N 7.61; 7.52 $C_{12}H_{12}BN$. Calculated %: C 79.60; H 6.68 B 5.97; N 7.73.

Molecular weight: found, 187, 185.7; Calculated, 181.

Di-α-naphthylaminoborine (VIII), Ar = α-$C_{10}H_7$. A stream of ammonia was passed for 30 minutes into a benzene solution of 1.8 g of the n-butyl ester of di-α-naphthylthioborinic acid. A slight evolution of heat was observed. A part of the benzene was distilled from the reaction mixture, and isopentane was added. There was obtained 1 g (70%) of di-α-naphthylaminoborine with an m.p. of 113-114°.

Found %: B 3.55; 3.99; N 4.97; 4.96 $C_{22}H_{16}BN$. Calculated %: B 3.84; N 4.98.

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TELOMERIZATION OF ETHYLENE WITH CARBON TETRACHLORIDE, CHLOROFORM, AND ETHYL TRICHLOROACETATE IN THE PRESENCE OF IRON PENTACARBONYL

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As was found by one of the authors of the present article, A. N. Nesmeyanov and E. Ts. Chukovskaya, iron pentacarbonyl is an initiator for the addition of silanes to olefins [1]. On the assumption that this is homolytic reaction, it appeared to us to be of interest to investigate the possibility of using iron pentacarbonyl as an initiator for the reaction of ethylene with polychlorohydrocarbons and certain of their derivatives. It was found that in the presence of iron carbonyl at a temperature of 100-130° and a pressure of 150-200 atm, ethylene smoothly undergoes telomerization with carbon tetrachloride and chloroform with the formation of $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes, in the first case, and α,α,α-trichloroalkanes, in the second. Closely similar values of the conversion of the polychloromethanes and of the ratios of the yields of individual telomer homologs were obtained in experiments carried out under comparable conditions but using iron pentacarbonyl or benzoyl peroxide as reaction initiators.

One patent discloses the telomerization of ethylene with ethyl trichloroacetate in the presence of benzoyl peroxide. The reaction resulted in a mixture of products, from which were separated compounds having the formula $Cl(CH_2CH_2)_nCCl_2CO_2C_2H_5$ in which $n = 1$ or 2. However, the patent gave no information on reaction conditions, conversion of trichloroacetate, or ratio of yields of the individual telomers. In the presence of iron pentacarbonyl the telomerization of ethylene with ethyl trichloroacetate proceeds smoothly and can be recommended as a preparative method for the synthesis of α,α,ω-trichlorocarboxylic acids containing an even number of carbon atoms in the molecule.

Attempts to carry out the reaction between ethylene and certain other compounds containing a trichloromethyl or a dichloromethyl group and also compounds containing a labile hydrogen atom were unsuccessful under the conditions studied.

EXPERIMENTAL PART

Telomerization of ethylene and carbon tetrachloride. 236 g of carbon tetrachloride and 0.5 ml of iron pentacarbonyl were charged to an 0.5-liter stainless steel rocker autoclave, and the autoclave was then pressured with ethylene to 80 atm. The mixture was heated to 95-100°, at which temperature the reaction began; completion of the reaction was indicated by the end of the pressure decrease. At this point, the reaction mixture was heated at the indicated temperature for another four hours.

After distillation of the unreacted carbon tetrachloride, the mixture of reaction products was fractionated, and the following fractions were collected:

I 58-62° at 22 mm, 8 g; II 89-99° at 15 mm, 60 g; III 75-106° at 4 mm, 46 g; IV 120-126° at 3 mm, 15 g; residue 23 g.

The following compounds were obtained by a second distillation of respectively, Fractions II, III, and IV

* The first fraction was not redistilled.

1,1,1,5-tetrachloropentane, 53 g, n_D^{20} 1.4870; d_4^{20} 1.3494; MR_f 44.54, MRcalc. 44.75; 1,1,1,7-tetrachloroheptane, 36 g, n_D^{20} 1.4840, d_4^{20} 1.2598, MR_f 54.05; MRcalc. 53.89; 1,1,1,9-tetrachloropropane, 11 g, n_D^{20} 1.4825; d_4^{20} 1.1981; MR_f 63.36; MR calc. 63.03.

The above constants are in general agreement with those usually cited for $\alpha,\alpha,\alpha,\omega$-tetrachloroalkanes.

Telomerization of ethylene with chloroform. The experiment was carried out in a manner analogous to that described above. 220 g of chloroform and 0.5 ml of iron pentacarbonyl were charged to the autoclave, and ethylene was introduced to a pressure of 50 atm. The reaction proceeded at a temperature of 130-140°. The reaction products from two experiments carried out under analogous conditions were combined. After distillation of the unreacted chloroform, the reaction mixture was distilled, and the following fractions were collected:

I, 40-80° at 68 mm, 17 g; II 75-86° at 67 mm, 32 g; III 76-106° at 9 mm, 30 g; IV, 52-81° at 2 mm, 27 g. Residue 56 g.

Fractions II, III, and IV* were distilled, and the following compounds were obtained:

1,1,1-trichloropentane, n_D^{20} 1.4540; d_4^{20} 1.1871; MR_f 40.03; MRcalc. 39.89; 1,1,1-trichloroheptane, n_D^{20} 1.4565; d_4^{20} 1.1221; MR_f 49.35; MR calc. 49.12; 1,1,1-trichlorononane, n_D^{20} 1.4580; d_4^{20} 1.0794; MR_f 58.55; MRcalc. 58.32.

The constants are in general agreement with those usually cited for 1,1,1-trichloroalkanes. The structure of these trichloroalkanes was confirmed for trichloroheptane, hydrolysis of which with concentrated sulfuric acid gave enanthic acid in good yield.

Telomerization of ethylene with ethyl trichloroacetate. The experiment was carried out in a manner similar to the preceding. 125 g of ethyl trichloroacetate and 0.5 ml of iron pentacarbonyl were charged to the autoclave, and ethylene was introduced to a pressure of 70 atm. The reaction proceeded at a temperature of 130-135°. After distillation of the unreacted ester, the following fractions were collected:

I, 45-70° at 8 mm, 35 g; II 70-93° at 8 mm, 37 g; III, 90-115° at 4 mm, 44g; IV, 117-130° at 3 mm, 10 g. Residue, 61 g.

The following were obtained by redistillation: 34 g of ethyl α,α,γ-trichlorobutyrate, b.p. 86-87° at 7.5 mm, n_D^{20} 1.4660; d_4^{20} 1.3068; MR_f 46.52; MR calc. 46.16; 42 g of ethyl α,α,ω-trichlorocaproate, b.p. 94-96° at 3 mm, n_D^{20} 1.4660; d_4^{20} 1.2465, MR_f 55.61; MR calc. 55.40; 6 g of ethyl α,α,ω-trichlorocaprylate, b.p. 111-112° at 1 mm, n_D^{20} 1.4720, d_4^{20} 1.1849; MR_f 65.13; MR calc. 64.63; accepted values for these constants may be found in references [2, 3].**

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Received April 2, 1959

* The first fraction was not redistilled.
** No reference [3] is given in Literature Cited.

ON THE DESTRUCTIVE CATALYTIC HYDROPOLYMERIZATION OF ISOBUTYLENE - HYDROGEN MIXTURES

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(Presented by Academician B. A. Kazanskii, April 22, 1959)

We have previously shown [1] that at a temperature of 190°, atmospheric pressure, and in the presence of a catalyst for the hydrocondensation of carbon monoxide with olefins (Co-clay), isobutylene, in contrast to n-butylenes, polymerizes, but to a very slight extent; the yield of liquid polymerizate comprised 2-5 % of the olefin charged. It was simultaneously noted that the addition of hydrogen to the isobutylene brought about a sharp increase in the yield of liquid polymerizate; the yield of polymerizate increased twofold with the addition of 0.2% hydrogen. The maximum yield of polymerizate with respect to isobutylene charged was obtained from an equimolar hydrogen isobutylene mixture; it was 18% at initial catalyst activity and 12% after 15 hours of catalyst use.

This effect of hydrogen was not observed during polymerization of isobutylene in the presence of clay—the catalyst base—which, was more active for this reaction than the Co-clay catalyst.

The present work was devoted to a study of the effect of the concentration of hydrogen on the polymerization and hydropolymerization of isobutylene, both quantitatively and qualitatively, i.e., to determine whether the course of the reaction is changed with the formation of products differing not only in degree of saturation but also in carbon skeleton structure. For this purpose, products obtained under the same conditions from isobutylene-hydrogen mixtures differing in component ratio were compared.

EXPERIMENTAL PART

The experimental method and the apparatus were the same as those described previously [2]. The isobutylene was obtained by dehydrationof isobutyl alcohol (b.p. 107-108°; d_4^{20} 0.8019; n_D^{20} 1.3957) over aluminum oxide, and it was twice condensed while the uncondensed residue was pumped off under vacuum. Electrolytic hydrogen was used. All experiments were carried out at atmospheric pressure, a temperature of 190°, and a space rate of feed gas of 100 hours^{-1}. The glass reaction tube had a diameter of 10 mm. It was charged with 30 cc of precipitated Co-clay catalyst (1:2) [3], which was reduced with hydrogen at 450° for 5 hours.

Catalyzates from three isobutylene-hydrogen mixtures were obtained in long experiments: 1) isobutylene + + 0.3% hydrogen, 2) 75% isobutylene + 25% hydrogen, and 3) 50% isobutylene + 50% hydrogen. Individual portions of catalyst were used for each mixture, and these were regenerated with hydrogen at 450° for 5 hours after each 15-20 hours use. The catalyzates were dried and freed of gas (isobutylene and isobutane) and were then distilled in a column having an efficiency of 40 theoretical plates and packed with triangular copper coils; the catalyzates were processed either directly or after complete hydrogenation at room temperature in the presence of Pt on carbon promoted with H_2PtCl_6 [4].

Catalyzate from a mixture of isobutylene + 0.3% hydrogen. The yield of liquid polymerizate was 10.1% and 6.3% of the isobutylene fed, respectively, over the fresh surface and after the catalyst had been in operation for 15 hours.

42 g of the polymerizate (d_4^{20} 0.7054; n_D^{20} 1.4088) was distilled in the column. The fractions collected and their constants are presented in Table 1, while the distillation curve is shown as Figure 1, 1. As may be seen

TABLE 1

Fractions Obtained from Hydropolymerizates from Gaseous Mixtures.

Fraction No.	Boiling range, deg C	Yield, vol% of orig. polymerizate	d_4^{20}	n_D^{20}	Hydrocarbons
		Mixture of iso-C_4H_8 + 0.3% H_2			
1	96–100.5	5.0	0.6932	1.4024	C_7H_{14}, C_7H_{16}
2	100.5–102	55.0	0.7142	1.4110	2,4,4-Trimethyl-1-pentene
3	102–105	9.5	0.7203	1.4135	2,4,4-Trimethyl-2-pentene
4	105–178	16.2	0.7362	1.4210	
5	178–183	10.0	0.7672	1.4356	Triisobutylenes
6	Residue >183	1.9	—	1.4440	
		Mixture of 75% iso-C_4H_8 + 25% H_2 (hydrogenated)			
1	24.5–26	0.6	—	—	2-Methylbutane
2	26–28	4.2	0.6205	1.3540	
3	52–64	3.8	0.6546	1.3731	2-Methylpentane
4	74.5–90	3.2	—	1.3830	C_7H_{16}
5	90–99	5.3	—	1.3895	C_7H_{16}
6	99–99.5	58.9	0.6922	1.3915	2,2,4-Trimethylpentane
7	101–112.5	4.3	—	1.3959	C_8H_{18}
8	112.5–135	5.7	0.7124	1.4020	C_8H_{16}, C_8H_{18}
9	135–151	1.1	—	1.4080	C_8H_{16}
10	155–177	3.2	—	1.4190	
11	177–178	1.7	0.7584	1.4250	$C_{12}H$
12	178–188	3.0		1.4258	
13	188–195	4.4	—	1.4290	
Residue	>195	0.5	—	1.4438	
		Mixture of 50% iso-C_4H_8 + 50% H_2 (hydrogenated)			
1	27–30	20.0	0.6202	1.3540	2-Methylbutane
2	30–59	5.7	0.6471	1.3650	
3	60–61	22.8	0.6528	1.3710	2-Methylpentane
4	63.5–99	17.1	0.6802	1.3820	C_7H_{16}
5	99–126	18.2	0.7062	1.3978	C_8H_{18}
6	>126	7.2	—	1.4075	
	Loss	9.0			

from these data, the catalyzate contained 55% 2,2,4-trimethyl-1-pentene (Fraction 2, literature data [5]: b.p. 101.36°, n_D^{20} 1.4036; d_4^{20} 0.7150), ~ 10% 2,4,4-trimethyl-2-pentene (Fraction 3; literature data [5]: b.p. 104.85°, n_D^{20} 1.4160; d_4^{20} 0.7212) and 10% triisobutylenes (Fraction 5), apparently, judging from the constants, 4,4-dimethyl-2-neopentyl-1-pentene (b.p. 177.7–178°, n_D^{20} 1.4297; d_4^{20} 0.7599) [5] and 2,4,4,7-tetramethyl-2-octene (b.p. 181°; n_D^{20} 1.4375; d_4^{20} 0.7685). Thus, the catalyzate contained more than 75% diisobutylenes and triisobutylenes, and was very close composition-wise to the product obtained by us previously [1] by ionic polymerization of isobutylene over a clay catalyst; this product contained 80% di- and triisobutylenes.

Catalyzate from a mixture of 75% isobutylene and 25% hydrogen. The yield of liquid hydropolymerizate comprised 13.6% and 6.7% of the isobutylene charged over the fresh surface and after 15 hours of catalyst operation, respectively.

The hydropolymerizate (d_4^{20} 0.7041; n_D^{20} 1.4083, bromine number 111.3, unsaturated hydrocarbon content 78%) had, after hydrogenation, d_4^{20} 0.6909, n_D^{20} 1.3979, bromine number 0.0. 100 ml of the hydrogenated product was distilled in the column. The fractions collected and their constants are presented in Table. Fractions for which the yield was less than 0.3% are not shown in the table. The distillation curve is shown as Figure 1,2. It may be seen from these data that almost 60% of the hydrogenated product consisted of isobutylene hydrodimer-2,2,4-trimethylpentane -(Fraction 6, literature data [5]: b.p. 99.24°, n_D^{20} 1.3915; d_4^{20} 0.6919), and about 5% was hydrotrimer (Fractions 11 and 12). The third plateau on Curve 2 (b.p. 177–175°) corresponds to 2,2,4,6,6-pentamethylheptane which corresponds to the olefin, 4,4-dimethyl-2-neopentene, mentioned above. Thus, it

TABLE 2

Fractions Obtained from the Hydropolymerizate from a Gas Mixture of 50% Iso-C_4H_8 and 50% H_2

Fraction No.	Boiling range, deg C	Yield, vol. % of orig. hydropolymerizate	d_4^{20}	n_D^{20}	Bromine No.	Unsaturates content, vol. %	C_n
1	20—41	29,6	0,6161	1,3591	39,0	17,5	C_5
2	41—72	25,0	0,6538	1,3750	41,8	22,3	C_6
3	72—99	15,7	0,6831	1,3900	35,9	22,4	C_7
4	99—125	13,2	0,7079	1,4015	51,7	24,3	C_8
5	Residue >125	4,9	—	1,4100	120,5	—	—
	Loss	11,6					

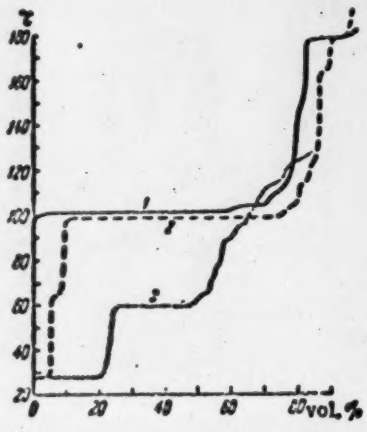

Fig. 1. Distillation curves for hydropolymerizates from gaseous mixtures: 1) Iso-C_4H_8 + 0.3% H_2; 2) 75% Iso-C_4H_8 + 25% H_2; 3) 50% Iso-C_4H_8 + 25% H_2.

may be assumed that the original polymerizate contained about 65% dimers and trimers of isobutylene. This decrease in the yield of isobutylene polymers in comparison with the preceding polymerizate (from the mixture of isobutylene + 0.3% hydrogen) was compensated by lower-boiling products, C_5-C_7, the yield of which comprised 17% of the hydrogenated product. It is interesting to note that methylalkanes were present among these hydrocarbons: 2-methylbutane (Fraction 1 and 2, first plateau on Curve 2 of Figure 1, literature data [5]: b.p. 27.85°, n_D^{20} 1.3537, d_4^{20} 0.6197), and 2- and 3-methylpentanes Fraction 3, break in the curve; literature data for 2-methylpentane: b.p. 60.27°, n_D^{20} 1.3715; d_4^{20} 0.6532; for 3-methylpentane: b.p. 63.28°, n_D^{20} 1.3765, d_4^{20} 0.6643). Fraction 8 was apparently a methylheptane boiling at 117-118°; there is a break in the distillation curve in this interval.

Thus, the addition of 25% hydrogen to the isobutylene led to the formation of intermediate hydrocarbons, chiefly monomethylalkenes and alkanes, in addition to polymers and hydropolymers which are multiples of isobutylene.

Catalyzate from a mixture of 50% isobutylene and 50% hydrogen. The yield of hydropolymerizate comprised 18 and 12% of the isobutylene charged, respectively, over the fresh surface and after 15 hours operation of the catalyst. 35 ml of the hydropolymerizate (d_4^{20} 0.6432, n_D^{20} 1.3870) was distilled in the column. The fractions collected and their constants are presented in Table 2. Part of the hydropolymerizate was completely hydrogenated, and 28 ml of the hydrogenated product (d_4^{20} 0.6389; n_D^{20} 1.3752) was distilled in the column. The fractions collected and their constants are presented in Table 1, and the distillation curve is shown as Figure 1, 3. It is seen from the data of Table 2 that the hydropolymerizate was a rather highly hydrogenated product, more than 3/4 of which was saturated hydrocarbons. It may be concluded from the data of Table 1 and Figure 1, 3 that the hydropolymerizate contained no diisobutylenes, triisobutylenes, or their hydrogenated products. The two larger plateaus on Curve 3 correspond to 2-methylbutane and 2-methylpentane, which comprised 20 and 30%, respectively, of the hydropolymerizate (Fractions 1 and 3). In addition, the hydropolymerizate contained 17% C_7H_{16} hydrocarbons and 18% C_8H_{18} hydrocarbons, which, judging from the constants, were only slightly branched.

The results presented show that at 190° and atmospheric pressure over a Co-clay catalyst, the course of polymerization and hydropolymerization of isobutylene in the presence of hydrogen depends on the concentration of the latter in the feed mixture. Moreover, it is possible to distinguish two extreme courses: 1) polymerization of isobutylene with the formation chiefly of diisobutylenes and triisobutylenes and their hydrogenation products, the reaction proceeding in the absence of, or at low concentrations of, hydrogen; 2) the formation of methylalkanes and methylalkenes with the methyl radical located mainly at the second carbon atom (from the end of the carbon chain), the reaction proceeding with a hydrogen content of 50% in the feed mixture. Both forms of polymerization

proceed at intermediate hydrogen concentrations. It may be assumed that the first process has an ionic character and is due to the presence of the catalyst support - clay - which, as a natural aluminosilicate, has acid properties. The second reaction apparently has a radical character and is due to the presence of reduced cobalt. As may be seen from the nature of the initial and final reaction products, this reaction is not a polymerization or hydropolymerization in the narrow sense of the word, since neither diisobutylene nor triisobutylene nor their hydrogenation products are formed, and destructive hydrogenation processes acquire important significance at various stages of the reaction. Therefore, this reaction, which has now been observed for the first time at such a low temperature and pressure, can be defined as destructive hydropolymerization of isobutylene under the influence of hydrogen. The mechanism of this reaction is the subject of our future investigations.

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* In Russian.

ON THE SYNTHESIS OF DIHYDRIC ALCOHOLS OF THE SILOXANE SERIES

1. THE INTERACTION OF CHLOROMETHYLDIMETHYLCHLOROSILANE AND BIS(CHLOROMETHYL)TETRAMETHYLDISILOXANE WITH SODIUM GLYCOLATE

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The present work was devoted to an attempt to synthesize dihydric alcohols of the siloxane series. With this aim, the interaction of chloromethyldimethylchlorosilane with sodium glycolate with subsequent conversion of the reaction product to bis(β-hydroxyethoxymethyl) tetramethyldisiloxane was studied.

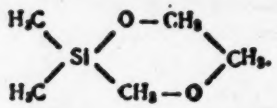
The reaction would be expected to proceed according to:

$$ClCH_2Si(CH_3)_2Cl + NaOCH_2CH_2OH \rightarrow HOCH_2CH_2OCH_2Si(CH_3)_2OCH_2CH_2OH \xrightarrow{H_2O}$$

$$\rightarrow HOCH_2CH_2OCH_2Si(CH_3)_2OSi(CH_3)_2CH_2OCH_2CH_2OH. \quad (I)$$

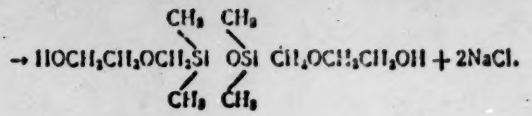
However, the course of the reaction proved to be more complex.

During the study of this reaction, it was found that substitution of a glycol radical for a chlorine proceeds readily both for a chlorine bound to the silicon and for chlorine in the chloromethyl group. A brief heating at 100° brings about 95% replacement of the halogens, as determined from the sodium chloride formed. However, β-hydroxyethoxymethyldimethyl-β-hydroxyethoxysilane was not found during an investigation of the reaction products, but a substance with a relatively low boiling point was obtained, the elemental composition and properties of which in all experiments corresponded to a compound of the formula



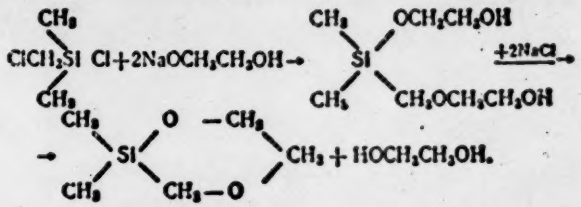
The attempt to carry out the reaction according to the above scheme failed, and an attempt was made to carry out the reaction of bis (chloromethyl) tetramethyldisiloxane with sodium glycolate:

$$ClCH_2Si(CH_3)_2OSi(CH_3)_2CH_2Cl + 2NaOCH_2CH_2OH \rightarrow \quad (II)$$

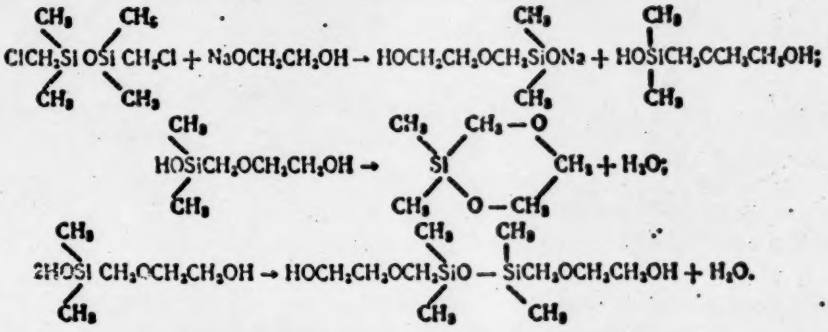


In this case too, substitution of both halogens proceeded readily, and 95% substitution has occurred after two hours at 100°. Analysis of the reaction products showed that the major product of this reaction was also a low-boiling product, the analysis of which corresponded to the analysis of the product obtained in the first synthesis. It was found that if the second stage of the synthesis (the introduction of the organosilicon component into the sodium glycolate) was carried out at a temperature of 80-100°, the formation of the indicated heterocyclic compound was the predominant reaction, while if the second component was introduced at a temperature of 140-150°, then approximately equal amounts of the cyclic derivative and bis (β-hydroxyethoxymethyl) tetramethyldisiloxane were formed.

In the case of the reaction with chloromethyldimethylchlorosilane, the formation of the heterocyclic derivative obviously can be explained by the formation of β-hydroxyethoxymethyldimethyl-β-hydroxyethoxysilane which then cyclizes to the indicated derivative with the liberation of a molecule of glycol:



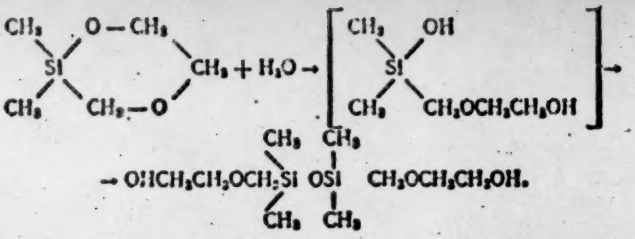
However, we were unable to isolate the intermediate β-hydroxyethoxymethyldimethyl-β-hydroxyethoxysilane. Both in the case of the reaction of the chlorosilane and in the case of the reaction with the disiloxane, the filtrate obtained from the separation of the precipitated sodium chloride distilled in the interval 120-195°, while the β-hydroxyethoxysilane should boil considerably higher. In the interaction of sodium glycolate with bis (chloromethyl) tetramethyldisiloxane, the formation of the heterocyclic derivative probably proceeds in a more complex manner:



Such a course of the reaction—through the formation of the silanol—which is explained by the presence of traces of moisture, is also possible in the case of chloromethyldimethylchlorosilane.

It was later established that the cyclic product obtained during the reaction, which boils at 138° and which is readily hydrolyzed to bis (hydroxyethoxymethyl) tetramethyldisiloxane, polymerizes with an increase in viscosity and molecular weight on standing under ordinary conditions in a flask closed by a ground-glass stopper. An investigation of the kinetics of this reaction is currently being carried out by measuring the change in viscosity, molecular weight, and hydroxyl-group content.

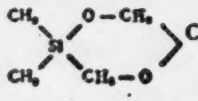
A study of the low-boiling product showed that it is easily hydrolyzed by a 1% solution of HCl at 60°, being converted to bis (β-hydroxyethoxymethyl) tetramethyldisiloxane in quantitative yield according to the reaction:



EXPERIMENTAL PART

I. The interaction of chloromethyldimethylchlorosilane with sodium glycolate. The reaction was made in a three-necked flask fitted with a stirrer, a thermometer, a reflux condenser, and a dropping funnel. 100 ml of freshly distilled ethylene glycol was placed in the flask and heated to a temperature of ~50° ; the flask heater was then switched off, and 9.2 g (0.4 mole) of fine pieces of metallic sodium was introduced, the temperature in the flask rising to about 60-65° due to the exothermic heat of reaction. As further portions of sodium were introduced, it was necessary to heat the reaction mixture periodically to cause the sodium to enter into the reaction more rapidly. The maximum temperature of the mixture was 100-105°. The resulting solution of sodium glycolate in glycol was cooled to 50° ; 28.6 g (0.2 mole) of chloromethyldimethylchlorosilane was added dropwise. The heat liberated during the addition raised the temperature of the mixture to 68°. After all of the chlorosilane had been added, the reaction mixture was heated for 6 hours at temperature of 95-100°. The resulting precipitate was filtered. The weight of the precipitate was 23.08 g (theoretical, 23.4 g). The chlorine content of the precipitate was 57 (calculated for NaCl, 60.6%).

The filtrate was extracted with benzene and then with ethyl ether, (to complete extraction), and the extract was distilled at atmospheric pressure. The extract distilled to dryness in the interval 100-195°. A second distillation gave 7.85 g of a product which corresponded in composition to a compound of the structure:



Yield 30%. B.p. 136-138°. n_D^{20} 1.4290; d_4^{20} 0.977; MR_f 34.82 ; $MR_{calc.}$ 35.29.

Found%: C 44.99; 44.82; H 9.30; 9.10; Si 20.46; 20.61 $C_5H_{12}OSi$. Calculated %: C 45.4; H 9.1; Si 21.2.

Molecular weight: found, 128; calculated, 132.

An additional 7 experiments were carried out under analogous conditions; the yield of cyclic product was 30-35%.

For proof of the structure of this cyclic derivative, the compound was subjected to hydrolysis by an equal weight of water containing 1% HCl. The mixture was heated for 1 hour at 60°, after which the hydrolysis product was extracted with ethyl ether, and the extract was dried with sodium sulfate and distilled under vacuum. 29.4 g of the cyclic derivative was obtained from several experiments, and this material was hydrolyzed and distilled to obtain two main fractions: 70-71° at 4 mm and 130-133° at 2 mm. The first fraction separated into two layers, the upper layer having an n_D^{20} of 1.4270 while that of the lower layer was 1.4380; i.e., the fraction contained a mixture of cyclic and bicyclic derivatives. Analysis of the fraction boiling at 130-133°/2 mm gave the following results:

Found%: C 42.00; 42.07; H 9.22; 9.27; Si 19.88; 19.68 $C_{12}H_{32}O_5Si_2$. Calculated %: C 42.55; H 9.21 ; Si 19.85.

Molecular weight: found, 285 ; calculated, 282 ; n_D^{20} 1.4440; d_4^{20} 1.013 ; MR_f 74.05 ; $MR_{calc.}$ 74.07. The % OH was 12.35 (calculated 12.05) ; i.e., hydrolysis of the cyclic derivative obtained from the above reaction led to the formation of bis (β-hydroxyethoxymethyl) tetramethyldisiloxane.

II. The interaction of sodium glycolate with bis(chloromethyl)tetramethyldisiloxane. The preparation of the sodium glycolate was carried out under the conditions described above. 18.4 g (0.8 mole) of sodium and 200 ml of ethylene glycol were used. The bis(chloromethyl)tetramethyldisiloxane, 92.0 g (0.4 mole), was introduced dropwise at a temperature of 80° . A precipitate gradually formed; the mixture was heated for 6 hours at 100° .

and the precipitate was then filtered. The weight of the precipitate was 40.6 g. The chlorine content was 56.3%. The filtrate was extracted with ethyl ether, and the extract was distilled at atmospheric pressure. All of the extract distilled within the interval 90-197°, and all fractions separated into two layers.

Hydrolysis of a mixture of all fractions by the method described above gave 46.6 g of bis(β-hydroxyethoxymethyl)tetramethyldisiloxane, which boiled at a temperature of 149-150° at 5 mm; n_D^{20} 1.4430; % OH, 11.32 (calculated, 12.05).

III. Synthesis of bis(β-hydroxyethoxymethyl)tetramethyldisiloxane without the separation of the cyclic derivative. The synthesis was carried out in a manner similar to that described above. 23.6 g (0.2 mole) of chloromethyldimethylchlorosilane was added dropwise to the sodium glycolate, which was obtained from 9.2 g (0.2 mole) of metallic sodium and 100 ml of glycol. The resulting precipitate was filtered. The weight of the precipitate was 21.4 g. The Cl content was 57.8 %. All of the filtrate (124.5 g), together with an equal amount of water, was returned to the flask, the mixture was acidified to a weakly acid reaction by the addition of concentrated hydrochloric acid, and it was then heated at 60-65° for 3 hours. After the mixture had cooled, it was extracted with ethyl ether, and the extract, after distillation of the ether, was distilled under vacuum. The aqueous layer was evaporated to dryness in an evaporating dish. The residue on the bottom of the dish weighed 7.9 g; the chlorine content of this residue was 46.9%. Distillation of the ether layer gave 10.0 g of bis(β-hydroxyethoxymethyl)-tetramethyldisiloxane, which boiled at 138-140°/3 mm; the yield was 35.4% of theoretical; n_D^{20} 1.4425; % OH, 11.5. In one of the experiments, the disiloxane was added to the sodium glycolate at 140°, and a precipitate slowly formed. After the introduction of the disiloxane, the mixture was heated for an additional two hours at 140-150°, after which it was filtered, the filtrate was extracted with benzene, and the extract was distilled.

23 g (1 mole) of sodium, 115 g (0.5 mole) of bis(chloromethyl)tetramethyldisiloxane, and 200 ml of glycol were used in the reaction. All of the fractions collected during distillation of the benzene extract at atmospheric pressure consisted of two immiscible liquids. It was assumed that the presence of the glycol could cause such a separation of the distillates. In order to confirm this assumption, all of the fractions (total weight 119.9 g) were combined, and to the mixture was added 100 ml of benzene and 20 ml of water to dissolve the glycol. The benzene layer was removed, dried, and again distilled under vacuum.

This distillation gave 41.4 g (29.3% of theoretical) of bis(β-hydroxyethoxymethyl)tetramethyldisiloxane b.p. 166°/15 mm, n_D^{20} 1.4425, and 22.5 g (17.0% of theoretical) of the cyclic product, b.p. 60°/18 mm, n_D^{20} 1.4250.

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THE ADDITION OF PHENYLPHOSPHINE TO UNSATURATED COMPOUNDS

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The addition of phosphine and of primary and secondary phosphines to unsaturated compounds has been studied only to slight extent up to the present time.

Stiles, Rust, and Vaughan [1] observed that phosphine adds to unsaturated compounds (1-butene, cyclohexene, allyl alcohol, allylamine) under the catalytic influence of light or organic peroxides. Similar reactions have been described in an English patent [2]. Mann and Miller [3] studied the cyanoethylation of phenylphosphine and diphenylphosphine by acrylonitrile. In 1959, there appeared a paper by Rauhut, Hechenbleikner, Currier, Schaefer, and Wystrach [4] describing their work in which they carried out a more detailed study of the addition of phosphine and phenylphosphine to acrylonitrile. During the course of the past few years, we have studied the addition of phenylphosphine to unsaturated compounds with the aim of obtaining bifunctional compounds containing phosphorus.

A brief report of the results of this work is presented in the present communication. As our experiments showed, phenylphosphine readily adds, in the absence of a catalyst, to esters of acrylic and methacrylic acids when the reactants are heated. In addition to phenylphosphine addition products, there also appeared small amounts of the corresponding phosphine oxides, which resulted from the oxidation of the tertiary phosphines formed by the addition reaction. The addition of phenylphosphine to allyl alcohol proceeds under the influence of catalysts which produce free radicals (azobisisobutyronitrile).

The reaction can be represented by the following equation:

$$C_6H_5PH_2 + 2CH_2=\overset{R'}{\underset{|}{C}}-R \rightarrow C_6H_5P\left(CH_2-\overset{R'}{\underset{|}{C}}H-R\right)_2,$$

where $R-COOCH_3$, $COOC_2H_5$, $COOC_3H_7$, $COOC_4H_9$, CH_2OH; $R'-CH_3$ or H.

The compounds obtained and their constants are given in Table 1.

With the aim of preparing different derivatives, we repeated the experiments of Mann on the addition of phenylphosphine to acrylonitrile, and we obtained β-cyanoethylphenylphosphine, di(β-cyanoethyl)phenylphosphine and its oxide. The constants of these compounds are presented in Table 2. By reduction of the di(β-cyanoethyl) phenylphosphine with lithium aluminum hydride, we obtained di(β-aminopropyl)phenylphosphine (see Table 2). Being derivatives of trivalent phosphorus, the tertiary phosphines were readily oxidized by atmospheric oxygen to the corresponding phosphine oxides, and they also added sulfur. The constants of some of the phosphine oxides and sulfides prepared are presented in Table 2.

We also carried out the interaction of phenylphosphine with acrolein, methacrylic acid, ethylene oxide, and allyl bromide.

TABLE 1

Compound	B. p., deg C/mm	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.	P,% found	P,% calc.	Yield, %
$C_6H_5P(CH_2-CHCOOCH_3)(CH_2-CHCOOCH_3)$ with CH_3	139–140/1,5	1,1016	1,5242	86,1	86,03	10,19	10	56,6
$C_6H_5P(CH_2-CH\,COOC_2H_5)(CH_2-CH\,COOC_2H_5)$ with CH_3	150–151°/1	1,0764	1,5172	94,99	95,27	9,33	9,14	57,8
$C_6H_5P(CH_2-CH\,COOC_3H_7)(CH_2-CH\,COOC_3H_7)$ with CH_3	170–171°/1	1,0394	1,5061	104,80	104,51	8,72	8,47	64,6
$C_6H_5P(CH_2-CH\,COOC_3H_7\text{-iso})(CH_2-CH\,COOC_3H_7\text{-iso})$ with CH_3	152–153°/1	1,0394	1,5038	104,20	104,51	8,77	8,47	65,7
$C_6H_5P(CH_2-CH\,COOC_4H_9)(CH_2-CH\,COOC_4H_9)$ with CH_3	185–186°/1	1,0267	1,5038	113,6	113,74	8,03	7,87	66,9
$C_6H_5P(CH_2-CH\,COOC_4H_9\text{-iso})(CH_2-CH\,COOC_4H_9\text{-iso})$ with CH_3	178–179°/1	1,0181	1,5001	113,90	113,74	7,93	7,87	76,1
$C_6H_5P(CH_2CH_2COOCH_3)(CH_2CH_2COOCH_3)$	149–150°/1	1,1388	1,5361	77,23	76,90	11,06	10,99	55,5
$C_6H_5P(CH_2CH_2CH_2OH)(CH_2CH_2CH_2OH)$	175°/1	1,1017	1,5740	67,69	67,30	3,76	13,71	56,16

EXPERIMENTAL PART

The phenylphosphine was prepared by the method of Freedman and Doak [5] and had a b.p. of 48.5–49° 15 mm.

Addition of phenylphosphine to esters of acrylic and methacrylic acids. 13.5 g of methyl acrylate and 6.1 g of phenylphosphine were placed in a four-necked flask fitted with a stirrer, a reflux condenser, and a thermometer. The reaction was carried out in an atmosphere of nitrogen. The flask was heated to 120–130° over a period of 6 hours. 8.6 g (55.5% of theoretical) of a product with a b.p. of 149–150°/1 mm, n_D^{20} 1.5361; d_4^{20} 1.1388, was obtained by distillation.

The addition of phenylphosphine to esters of methacrylic acid was carried out in a similar manner.

Addition of phenylphosphine to allyl alcohol. The reaction was carried out in a manner similar to the preceding. 10.7 g of phenylphosphine, 15 g of allyl alcohol, and 0.1 g of azobisisobutyronitrile were heated for 7 hours at a temperature of 120–130°. 12.3 g (56.16% of theoretical) of a product with a b.p. of 175°/1 mm, n_D^{20} 1.5740; d_4^{20} 1.1017 was obtained by distillation.

Addition of phenylphosphine to acrylonitrile. The reaction was carried out by heating reactants in a flask fitted with a reflux condenser at 80–90° for 3 hours and at 120–130° for 6 hours. From 30.1 of phenylphosphine and 49 g of acrylonitrile was obtained 28.4 g (48.8%) of di(β-cyanoethyl)phosphine with a b.p. of 176.5–178° at 0.5 mm, 3.5 g (7.9%) of β-cyanoethylphosphine with a b.p. of 104°/0.5 mm, and 1.3 g (2.04%) of di(β-cyanoethyl) phosphine with a b.p. of 104–105°.

TABLE 2

Compound	M.p., deg C	B.p., deg C/mm	d_4^{20}	n_D^{20}	MRD found	MRD calc.	P,% found	P,% calc.	Yield,%
$C_6H_5P(CH_2CH_2CN)(CH_2CH_2CN)$	69,70	176,5—178/0,5	1,1043	1,5672	63,91	63,64	13,9	14,35	48,8
$C_6H_5P(CH_2CH_2CN)H$	—	104°/0,5	1,0710	1,5649	49,57	50,09	18,16	19,01	7,9
$C_6H_5P(O)(CH_2CH_2CN)(CH_2CH_2CN)$	104—105	235—240°/0,5	—	—	—	—	13,19	13,3	2,04
$C_6H_5P(CH_2CH_2CH_2NH_2)(CH_2CH_2CH_2NH_2)$	—	142—144°/1	1,0292	1,5728	71,69	71,099	13,67	13,83	48,5
Phosphine oxides and sulfides									
$C_6H_5P(O)(CH_2CH(CH_3)COOCH_3)(CH_2CH(CH_3)COOCH_3)$	—	184°/0,5	1,1712	1,5495	—	—	8,97	9,18	73,3
$C_6H_5P(O)(CH_2CH(CH_3)COOC_2H_5)(CH_2CH(CH_3)COOC_2H_5)$	—	177—178°/1	1,1128	1,5123	—	—	8,42	8,75	17,1
$C_6H_5P(O)(CH_2CH(CH_3)COOC_3H_7)(CH_2CH(CH_3)COOC_3H_7)$	—	182—183°/0,5	1,0686	1,5028	—	—	7,85	8,11	18,2
$C_6H_5P(O)(CH_2CH(CH_3)COOC_4H_9)(CH_2CH(CH_3)COOC_4H_9)$	—	205—270°/0,5	1,0780	1,5219	—	—	7,43	7,28	75,3

Preparation of di(γ-aminopropyl) phenylphosphine. An ether solution (300 ml) of 7.2 g of lithium aluminum hydride was charged to a flask fitted with a stirrer, an adapter, and a reflux condenser. A hypodermic syringe containing 10 g of di(β-cyanoethyl)phenylphosphine was fitted to the adapter. The contents of the flask were heated to boiling on a water bath, and the contents of the syringe were added to the solution. After decomposition of the complex with a 30% solution of NaOH, the ether layer was decanted and distilled. 5 g (48.5%) of di(γ-aminopropyl)phenylphosphine with a b.p. of 142-144°/1 mm was obtained.

Addition of sulfur to di(carbalkoxyisopropyl)phenylphosphine. The reaction was carried out in an atmosphere of nitrogen by heating the reactants at 120-130° for 3 hours. From 5.5 g of di(β-carbomethoxyisopropyl) phenylphosphine and 0.5 g of sulfur was obtained 4.4 g of thidi(β-carbomethoxyisopropyl)phenylphosphine with a b.p. of 184°/0.5 mm, n_D^{23} 1.5495; d_4^{23} 1.1712.

The addition of sulfur to di(β-carbobutoxyisopropyl)phenylphosphine was carried out in a similar manner.

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POLYCONDENSATION OF AMINOENANTHIC, AMINOPELARGONIC, AND AMINOUNDECANOIC ω-AMINO ACIDS IN THE SOLID PHASE

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Polycondensation of bifunctional compounds is generally carried out by heating the compoenents at temperatures exceeding their melting points and those of the corresponding linear polymers.

According to the literature, it is possible to carry out the polycondensation of certain bifunctional compounds in the solid state. Among such compounds are the hexamethylenediamine salt of adipic acid [1], ε-aminocaproic acid [2], ω-aminoundecanoic acid [3], the methyl ester of tetraglycine [4], and low molecular-weight products of the condensation of diethylolterephthalate [5]. The available information merely establishes the possibility of solid-state polycondensation of these substances. Up to the present, this has not been studied systematically.

Moreover, polycondensation in the solid state, which is an example of the quite rare reactions in which solid organic substances participate, is of great theoretical interest, and the reaction may find application in the technological production of polycondensation resins as a method for carrying out this reaction under milder conditions than those used in ordinary polycondensation in the melt. This has particularly great significance for inadequately stable monomers and their polymers.

In addition, solid-state polycondensation is apparently a basic method for the preparation of infusible polymers or polymers which melt with decomposition at high temperature, for example, polyamides containing aromatic or hydroaromatic [6] rings in the chain of the macromolecule. Such thermally stable polyamides may find very important application in engineering for special purposes.

Studying the general regularities of polycondensation in the solid state, we investigated the solid-state polycondensation of three aliphatic ω-amino acids—aminoenanthic, aminopelargonic, and aminoundecanoic and the effect on the process of temperature, nature of the amino acid, and other factors.

EXPERIMENTAL PART

The polycondensation of aliphatic ω-amino acids may be expressed by the following general equation:

$$n\text{-}H_2N(CH_2)_mCOOH \rightleftarrows H_2N(CH_2)_m-[CO(CH_2)_mNH-]_{n-1}COOH + (n-1)H_2O.$$

The kinetics of this reaction may be conveniently studied through the decrease in weight of the amino acid owing to the evolution of water. The apparatus used for continuously weighing the reacting substances has been described for measuring the rate of pyrolysis of polystyrene in a nitrogen atmosphere [7]. The nitrogen flow rate was the same in all experiments and amounted to 0.18 liters/minute. Constant temperature was maintained by means of a fused metal bath (Wood's metal), the temperature of which was automatically held constant with an accuracy of ± 0.5°. The accuracy of the weighings was ± 1 mg.

Clearly, unequivocal results from a study of the kinetics of the polycondensation reaction can be obtained by this method only in case there are no other reactions, such as cyclization of the amino acids with the formation of lactams or splitting out of volatile compounds other water. Of the homologous series of aliphatic ω-amino acids acids having more than six methylene groups in the molecule satisfy this condition.

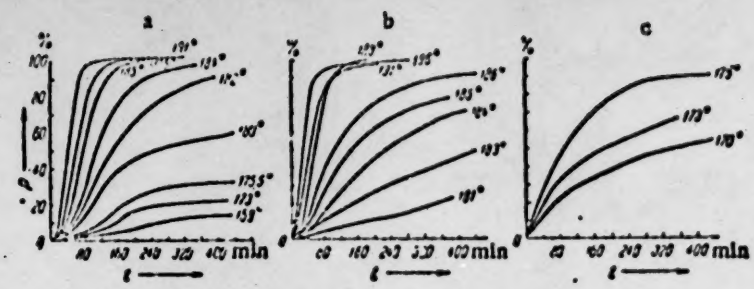

Fig. 1. Kinetics of the polycondensation of amino acids: a) aminoenanthic acid, b) aminopelargonic acid; c) aminoundecanoic acid.

TABLE 1

Polycondensation of Aminoenanthic Acid at 184°

Expt. No.	Time, hr	Yield of polyamide P, %	Spec. Vis. of 0.5% solution of polyamid in tricresol	Mol. wt. of polyamide from NH_2	d.p. from NH_2	Amt. of H_2O calc. from d.p. and P, g/g amino acid	Amt. H_2O, measured, g/g amino acid
1	1	18	0,11	1480	12	0,021	0,025
2	2	58	0,25	4000	32	0,070	0,072
3	4	90	0,34	5870	46	0,109	0,112
4	6	98	0,48	6950	55	0,119	0,121
5	8	100	0,58	8250	65	0,122	0,124
6	18	100	0,65	—	—	—	—

We used amino acids prepared from tetrachloroalkanes, products of the telomerization of ethylene with carbon tetrachloride [8], namely, aminoenanthic, aminopelargonic, and aminoundecanoic acids.

Technical amino acids of a high degree of purity were subjected to an additional recrystallization, following which their melting points were: 193-194° for aminoenanthic acid, 191-192° for aminopelargonic acid, and 181-182° for aminoundecanoic acid. According to elemental analyses, these amino acids were the pure products.

When the amino acids were heated close to their melting points (1-5° below), polycondensation proceeded partly in the liquid phase; this resulted in the formation of a block of solid polyamide (the melting points of the polyamides from aminoenanthic, aminopelargonic, and aminoundecanoic acids were, respectively, 225, 198, and 183°). At lower temperatures (5-20° below the melting point), heating of the amino acids converted them to a solid, white, porous mass, or else they remained in the form of powders. At still lower temperatures, the rate of polycondensation became practically unmeasurable, since it was very low.

Kinetic curves for the polycondensation of the amino acids in the solid state are shown in Figure 1, where P is the degree of completion of the reaction (yield of polymer) in weight per cent.

The reproducibility of the experiments was satisfactory, since when several polycondensation experiments were carried out at the same temperature, the values of the degree of completion varied within the limits of 1 to 3%.

The values of the degree of completion of the polycondensations of the amino acids as determined by measuring the amounts of water evolved are in good agreement with the values determined from the polymer yields (extraction of the polycondensation products with water to remove the water-soluble amino acid) and with those determined from the content of terminal amino groups in the polycondensation products. The content of terminal amino groups was determined by potentiometric titration of a solution of the polyamide in a mixture of phenol, alcohol, and water with a 0.1 N solution of hydrochloric acid [9].

From the values of the degree of polymerization (d.p.) of the polyamides as determined from the number of terminal groups, and from the polymer yields, it is possible to calculate the amount of water evolved from a

TABLE 3

Activation Energies for the Polycondensation of Aminoenanthic, Aminopelargonic, and Aminoundecanoic Acids

Expt. No.	Temp., deg C	Max. Rate, W, nominal units	lg W	E, cal.	Notes
Aminoenanthic acid					
1	180	70	1,845	92 000	Solid-phase reaction
2	182	120	2,079		
3	184	180	2,255		
4	185	220	2,343	43 000	In the presence of liquid phase
5	187,5	260	2,415		
6	191	360	2,556		
Aminopelargonic acid					
1	193	35	1,544	180 000	Solid-phase reaction
2	184	65	1,813		
3	185	110	2,041		
4	186	160	2,204		
5	188	290	2,462	38 000	In the presence of liquid phase
6	191	400	2,602		
7	196	570	2,756		
Aminoundecanoic acid					
1	170	70	1,845	60 000	Solid-phase reaction
2	173	100	2,000		
3	175	150	2,176		

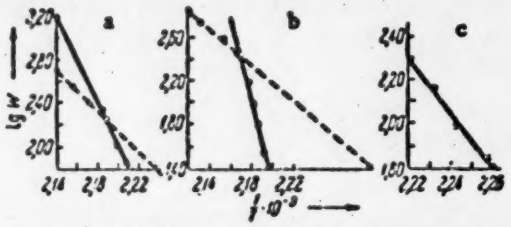

Fig. 2. Activation energies of the polycondensation of amino acids in the solid phase and in the presence of a liquid phase: a) aminoenanthic acid; b) aminopelargonic acid; c) aminoundecanoic acid.

specific amount of amino acid through the use of the equation for the polycondensation of amino acids.

A comparison of these values with the amounts of water determined by direct weighing are presented in Table 1.

It may be seen upon consideration of Table 1 that that the amounts of water determined by direct weighing and the values found from the d.p. values and from the polymer yields are in satisfactory agreement within the limits of experimental error.

It follows from the experimental data that:

1. Polycondensation of aminoenanthic, aminopelargonic, and aminoundecanoic acids takes place in the solid phase at an appreciable rate within rather narrow temperature intervals (6-15°) lying close to the melting points of these amino acids (5-20° below) and close to the melting points of the corresponding polyamides (8-50° below).

2. The polycondensation rate has a very high temperature coefficient.

3. In order to obtain from aminoenanthic acid polyamides with the specific viscosity in triecresol required for the forming of strong fibers, the reaction time in the solid state at 184° must be not less than 18 hours.

4. A comparison of the solid-state polycondensation rates of the three amino acids at the same temperature cannot be made owing to the difference in the temperature intervals in which polycondensation of aminopelargonic and aminoundecanoic acids takes place. Moreover, such a comparison does not take into account how close the polycondensation temperature is to the melting point of the amino acid. If the polycondensation rates are compared at temperatures removed the same number of degrees from the melting points of the amino acids, the amino acids

may be arranged in the following order with respect to polycondensation rate: aminoenanthic (185°) > aminoundecanoic (173°) > aminopelargonic (183°).

If the usual kinetic method is used to describe the solid-state reaction, then calculation of the effective activation energies yields the data presented in Table 2 and Figure 2.

The values of the effective activation energies were determined on the basis of the maximum rates of the polycondensation reactions. The maximum rates were taken from the maxima in curves showing the reaction rate as a function of time, which, in turn, were obtained by differentiation of the curves showing the variation in P, %, with time (Figure 1).

The amino acids may be arranged in the following order with respect to activation energy of the solid-phase polycondensation process: aminoundecanoic < aminoenanthic < aminopelargonic. There is no connection between this series and the chemical structures of the amino acids. As would be expected, the activation energy of the polycondensation process drops sharply when the reaction is carried out in the presence of a liquid phase.

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ON THE MECHANISM OF THE AMINATION OF CHLOROFLUOROBENZENES WITH METAL AMIDES AND AQUEOUS AMMONIA

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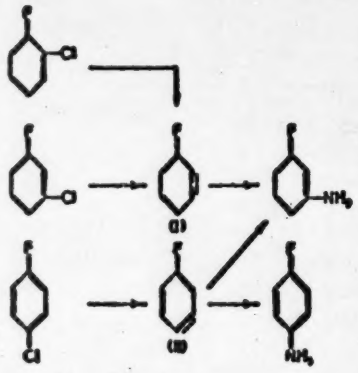
It is known that fluorobenzene [1] and fluorotoluene [2] do not react with alkali metal amides in liquid ammonia. The relative lability of halogen atoms in other aromatic monohalo derivatives during reaction with alkali metal amides in liquid ammonia generally increases in the series Cl, Br, I. Amination of compounds containing several different halogens remains almost unstudied. It is known only that by the action of potassium amide in liquid ammonia, p-bromofluorobenzene is converted, with 30% yield, to a mixture of m- and p-fluoroanilines in a ratio of 1:4 [3]. On the basis of patent data on the production of p-chloroaniline by the action of aqueous ammonia on p-bromochlorobenzene in the presence of copper salts [4], it may be concluded that in this reaction the lability of the halogen increases with its atomic weight.

We have studied the amination of chlorofluorobenzenes with alkali metal amides in liquid ammonia and also with aqueous ammonia in the presence of cuprous chloride. In all of the cases studied, the chlorine atoms were replaced by the amino group. In aminations with metal amides, the substitution of lithium or potassium amide for sodium amide had practically no effect on yield or composition of the amination products. The experimental results are presented in Table 1.

The fluoroanilines were analyzed by comparing the i.r. spectra of 1.5% solutions in carbon tetrachloride with the spectra of the pure compounds at wave lengths of 8.15 μ, 8.35 μ, and 8.80 μ for the ortho, meta, and para isomers, respectively. The spectra were taken with an IKS-14 spectrophotometer*. The acetyl derivatives of the fluoroanilines obtained in Experiments 1-4 and 6 were prepared, and these derivatives produced no depression of the melting point when mixed with acetyl derivatives of known compounds.



* The spectroscopic analyses were carried out by V. A. Plakhov.

According to our data, fluorobenzene undergoes practically no amination by aqueous ammonia in the presence of cuprous chloride (6 hours, 250°).

Amination by metal amides probably proceeds through the intermediate formation of substituted dehydrobenzenes [3]. Moreover, the same intermediate product (I) is obviously formed from o- and m-chlorofluorobenzenes, while (II) is formed from the para isomer.

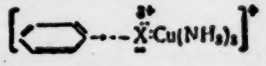
The isomer composition of the amination products confirms the assumption by Roberts and co-workers [3] of an influence of the inductive effect of electronegative substituents (fluorine in our case) on the direction of the addition of the NH_2^- ion to substituted dehydrobenzenes.

Previously, one of us and V. A. Kobelev [5] proposed a mechanism for the catalytic exchange of aromatic chlorine, which was based on kinetic data; according to this mechanism, the reaction is initiated by the addition of the catalyst to a molecule of the halogen derivative:

$$ArCl + Cu(NH_3)_2^+ \rightarrow [ArCl \cdot Cu(NH_3)_2]^+.$$

The halogen in this addition product is very labile, and it readily reacts further with ammonia with the formation of the amine.

The results of the interaction of chlorofluorobenzenes with aqueous ammonia in the presence of copper salts permits certain considerations as to the nature of the complex. The circumstance that the chlorine atom is selectively active in this reaction allows us to assume that the copper ammoniate cation interacts directly with the halogen atom. It is probable that the copper ion coordinatively adds to the unshared pair of electrons on the halogen:



In the complex, the halogen atom acquires a positive charge which weakens its conjugation with the ring, and the inductive effect increases. At the same time, the addition of a nucleophilic reagent to the carbon atom linked to the halogen and subsequent elimination of the halogen are facilitated. The difference in the reactivities of chlorine and fluorine atoms during catalytic ammonolysis of chlorofluorobenzenes is readily explained by such a structure for the complex. Obviously, the ease of addition of the copper ion to the halogen atom must be inverse to the electronegativity of the halogen. Consequently, the halogens may be arranged in the following series with respect to lability: $F \gg Cl < Br$.

It is possible that the high catalytic activity of salts of monovalent copper as compared to salts of divalent copper [6] is explained by the greater availability for coordination of the copper atom in the singly charged diammoniate than in the doubly charged tetraammoniate.

TABLE 1

Amination of Chlorofluorobenzenes

Expt. No.	Initial chlorofluorobenzene	Aminating agent	Yield of fluoroaniline, %	Isomer composition of fluoroanilines, %		
				ortho	meta	para
1	Ortho	$NaNH_2(NH_3)$	83	—	100	—
2	Ortho	$NH_{3aq}(CuCl)$	62	100	—	—
3	Meta*	$NaNH_2(NH_3)$	83	—	100	—
4	Meta	$NH_{3aq}(CuCl)$	64	—	100	—
5	Para	$NaNH_2(NH_3)$	53	—	20±3	80±3
6	Para	$NH_{3aq}(CuCl)$	75	—	—	100

* The first experiments on the interaction of m-chlorofluorobenzene with sodium amide were carried out by student A. N. Shikanov.

EXPERIMENTAL PART

1. Amination with metal amides. 20 g (0.15 mole) of chlorofluorobenzene was added to the metal amide, which was prepared in the usual manner [1] from 0.3 g-atoms of the alkali metal and 500 ml of anhydrous liquid ammonia. The mixture was stirred for 5 hours, and 24 g of ammonium nitrate was then added. The ammonia was evaporated, and the residue was treated with ether. The ether was distilled, and the fluoroaniline was then obtained from the residue by distillation.

2. Amination with aqueous ammonia. 5.86 g of chlorofluorobenzene, 0.5 g of cuprous chloride, and 50 ml of 31% aqueous ammonia were charged to a 200-ml rotating autoclave. The autoclave was heated for 6 hours at 250°. The organic material was extracted from the reaction mixture with ether (5 times with 20 ml portions). The ether solution was washed with water to a neutral reaction toward litmus and dried over sodium sulfate. The ether was distilled, and the fluoroaniline was obtained from the residue by distillation.

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THE EFFECT OF THE ADDITION OF ELEMENTS OF THE SECOND GROUP OF THE PERIODIC SYSTEM ON THE ACTIVITY OF CHROMIA-ALUMINA AROMATIZATION CATALYSTS

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We have previously shown that the alkali metal elements are promoters for chromia-alumina catalysts in the aromatization of cyclohexane and the dehydrocyclization of n-heptane [1].

In the present work, we found that the elements of the second group of the periodic system (with the exception of mercury, the addition of which to the catalyst was not tested) have a promoting effect on the aromatization of cyclohexane. This effect increases with an increase in atomic weight from beryllium to barium; the yield of benzene in the presence of the catalyst containing barium was about 88% calculated on the original cyclohexane (95% of that theoretically possible), which exceeds by approximately 18% the yield of benzene in the presence of the unpromoted catalyst.

The promoting effect of the elements of the second group on the dehydrocyclization of n-heptane was less than on the aromatization of cyclohexane, and was observed only for the alkaline earth elements. The addition of beryllium, magnesium, and zinc had practically no effect on the activity of the catalyst, and the addition of cadmium even decreased it somewhat.

EXPERIMENTAL PART

The methods of purification of the original hydrocarbons, the apparatus, the method of carrying out the experiments, and the methods of investigating the catalyzates have been described in a previous paper [1].

The original hydrocarbons had the following properties:

	B.p. (760 mm)	n^{20} *	d_4^{20}	F.p., °C
Cyclohexane	80.7	1.4260	—	+ 6.4
n-Heptane	98.4	1.3878	0.6834	—

In preparing the promoted catalysts, one of the preparations of chromia-alumina catalyst, preliminarily twice heated in a stream of air at 520°, was divided into portions of equal weight and volume. Each portion was impregnated with an aqueous solution of the nitrate of a metal of the second group, the amount of nitrate being that which would give a promoted catalyst of the following composition, in mole%, after thermal treatment of the catalyst: 1.3% oxide of the metal of the second group, 14.8 chromium oxide, and 83.9% aluminum oxide; the samples of unpromoted catalyst were impregnated with distilled water. In all cases, equal volumes of water were used for the impregnations. Complete solution of the barium nitrate was accomplished only with slight heating owing to the limited solubility of the barium nitrate. All samples were dried at 110-120° for 5 hours; 20 ml of catalyst was charged to the catalyst tube, after which it was heated in a stream of air to 520-530°.

Four-hour experiments with cyclohexane were carried out twice with each catalyst sample; the catalyst was regenerated after each experiment. The experiments were carried out at a temperature of 520° and a space rate of 0.35 $hours^{-1}$. The experimental results are presented in Table 1.

* As in original-Publisher.

TABLE 1

Aromatization of Cyclohexane. Temperature 520°; Space Rate 0.35 Hours^{-1}

Expt. No.	Promoter	n_D^{20} of catalyzate	Yield, wt. %, calc. on C_6H_{12}		
			catalyzate	aromatics	unsaturates
1	Without promoter	1.4812	88.2	69.2	—
2		1.4800	91.5	70.9	2.6
3	Be	1.4812	92.2	72.4	1.8
4	Be	1.4805	89.1	71.9	1.3
5	Mg	1.4790	89.1	66.6	1.3
6	Mg	1.4800	91.9	75.5	1.3
7	Ca	1.4795	89.8	74.1	0.9
8	Ca	1.4810	89.5	80.1	0.6
9	Sr	1.4790	93.0	68.4	1.5
10	Sr	1.4809	90.3	82.8	0.6
11	Ba	1.4809	91.1	75.6	1.1
12	Ba	1.4820	94.2	87.6	0.6
13	Zn	1.4790	92.9	67.3	2.2
14	Zn	1.4820	93.9	72.5	1.3
15	Cd	1.4758	92.5	66.1	1.9
16	Cd	1.4812	91.0	74.2	1.7

TABLE 2

Dehydrocyclization of n-Heptane. Temperature 530°; Space Rate 0.35 Hours^{-1}

Expt. No.	Promoter	n_D^{20} of catalyzate	Yield, wt. %, calc. on C_7H_{16}		
			catalyzate	aromatics	unsaturates
17	Without promoter	1.4760	76.0	59.0	7.4
18	The same	1.4810	85.1	62.2	7.9
19	The same	1.4801	85.1	61.3	8.2
20	Be	1.4800	81.6	63.2	7.5
21	Be	1.4792	80.5	61.6	5.8
22	Mg	1.4785	81.2	58.9	7.9
23	Mg	1.4805	81.6	59.8	7.9
24	Ca	1.4805	85.2	65.7	6.3
25	Ca	1.4815	85.1	65.2	—
26	Sr	1.4800	85.6	66.4	6.8
27	Sr	1.4810	85.7	69.4	4.8
28	Ba	1.4830	87.0	67.0	6.3
29	Ba	1.4801	85.2	64.2	5.6
30	Zn	1.4820	81.4	56.2	8.8
31	Zn	1.4801	85.7	69.6	6.0
32	Cd	1.4820	82.2	56.3	—
33	Cd	1.4810	83.8	57.0	—

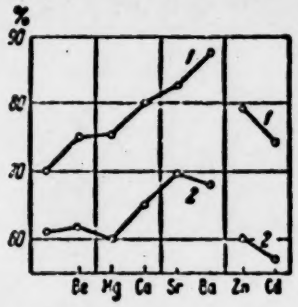

Fig. 1. Yields of aromatics from n-heptane and cyclohexane in the presence of chromia-alumina catalysts promoted with Group II metals: 1) dehydrogenation of cyclohexane; 2) dehydrocyclization of n-heptane.

In considering the data of Table 1, it should be noted that in the first of the two parallel experiments with each of the catalysts containing promoter, the yield of aromatics was less than in the second. A similar phenomenon was noted in our work on chromia-alumina catalysts promoted with the alkali elements [1,2].

Since the chromia-alumina catalyst was heated twice at 520° prior to deposition of the promoter, it is difficult to assume that this phenomenon was connected with a change in the surface and porosity of the catalyst structure during heating in the first experiment. It is more probable that it is connected with an interaction between the promoter and the remaining components of the catalyst during the experiment and regeneration. Therefore, in Figure 1, which compares the yields of aromatics obtained with catalysts with different promoters, the yields shown are those obtained in the second of the experiments with each catalyst, since the process of initial forming of the catalyst should affect the results of the second experiments to a lesser extent.

As seen from Table 1 and the yields of aromatics obtained with catalysts containing beryllium, magnesium, calcium, strontium, and barium, were higher by 5.5, 5.5, 10, 13, and 17.6%, respectively, than the yield obtained with the unpromoted catalyst.

That the yields obtained with the catalysts promoted with beryllium and magnesium were almost equal may, perhaps, be explained by experimental error, and the difference between them might have been greater had the experimental method been more accurate. The experiments with n-heptane were conducted with catalysts which had been regenerated twice after experiments with cyclohexane. The process of forming the catalysts had been concluded prior to the experiments with n-heptane, and, therefore, the results obtained with the same sample of promoted catalyst differed much less than in parallel experiments with cyclohexane, the deviation not exceeding the experimental error (2-4%). The temperature of the experiments was 530°, and the space rate was 0.35 hours^{-1}. The results are presented in Table 2.

From the data of Table 2 it follows that all of the alkaline earth elements are promoters for chromia-alumina catalysts for dehydrocyclization of n-heptane, but the effect is significantly less than in the aromatization of

cyclohexane. The increase in the yield of aromatics with the catalyst containing calcium was only about 4%, while that with the catalysts containing strontium and barium was 7-8%. The remaining elements exhibited no promoting effect.

The yields of unsaturates during aromatization of cyclohexane were very small and varied from 0.4 to 2.6% (Table 1). The yields of unsaturates were greater during dehydrocyclization of n-heptane and comprised 4.8-8.6% (Table 2). As a rule, for both reactions the yield of unsaturates was lower in those experiments in which the yield of aromatics was higher. A possible reason for this was considered in our previous paper [1].

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PHOTOMETRIC DETERMINATION OF THORIUM AND URANIUM WITH ARSENAZO III REAGENT

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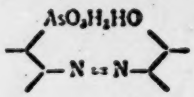
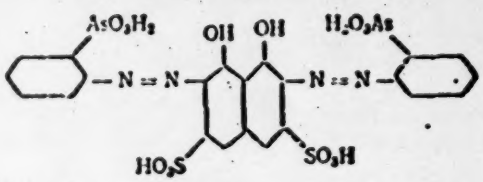
It has been pointed out in the literature that organic reagents containing a functional group of the form:



possess valuable analytical properties. Among such reagents are those proposed by V. I. Kuznetsov, thoron (2-phenylarsonic acid-< 1-azo-1 > -2-hydroxynaphthalene-3,6-disulfonic acid) [o-(2-hydroxy-3,6-disulfo-2-naphthylazo) benzenearsonic acid] [1], arsenazo I (2-phenylarsonic acid-< 1-azo-2 > -1,8-dihydroxynaphthalene-3,6-disulfonic acid) [o-1,8-(dihydroxy-3,6-disulfo-2-naphthylazo) benzenearsonic acid] [1], and arsenazo II (biphenyl-4,4'-diarsonic acid-3,3'-bis(< -azo-2> -1,8-dihydroxynaphthalene-3,6-disulfonic acid) [3,3'-bis(1,8-dihydroxy-3,6-naphthylazo)-4,4'-biphenylarsonic acid] [2], which have been widely used for the photometric determination of Th [3-6], U [7], Pu [8], and other elements.

We have synthesized the reagent 1,8-dihydroxynaphthalene-3,6-disulfonic acid-2,7-bis(< -azo-> -2-phenylarsonic acid), which we have named, for the sake of brevity, arsenazo III; this reagent also contains the indicated groupings:



Arsenazo III

At the appropriate pH values, this reagent gives clear, contrasting reaction with Th, U^{IV}, U^{VI}, the rare earths, Be, Pb, and certain other elements. The color changes from rose (reagent) to emerald green and blue.

A basic feature of arsenazo III which distinguishes it from previously described reagents is the ability to form with the cations of elements especially stable inner-complex compounds, the stability of which exceeds by several orders of magnitude the stability of complexes formed by arsenazo I or II. For this reason, determination of the elements becomes possible in strongly acid solutions and without the preliminary, usually quite lengthy, separation of sulfates, phosphates, fluorides, oxalates, and other interfering substances.

The relative stability of the complexes formed by arsenazo III and its analogs can be quantitatively characterized by the use of the "stability index method" - a method described by V. I. Kuznetsov [2]. The stability index (n) is a specific constant for the system reagent-element-masking complex former (at a given pH). It is found by purely experimental means, and its value (which can range from 1 to ∞) is determined by the ratio of the

TABLE 1

Comparative Stabilities of Complexes of Arsenazo and Its Analogs with U^{VI} and Th

Complex former	Arsenazo I	Arsenazo II	Arsenazo III
KH_2PO_4	125*/250	250/300	$>1\cdot10^6$ / $>1\cdot10^6$
KF	60/20	110/30	$>1\cdot10^6$ / $1\cdot10^3$
$H_2C_2O_4$	~2/~2	4,5/~6	500 / $2\cdot10^3$
Trilon B	60/1	100/1	$\gg1\cdot10^6$ / $\sim10^4-10^5$
Citric acid	15/~2	30/~4	$\sim5\cdot10^3$ / $>1\cdot10^6$
Tartaric acid	180/60	400/100	$>1\cdot10^7$ / $>1\cdot10^7$

* The figures above the line are for U^{VI}; those under the line are for Th.

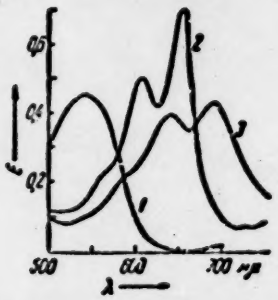


Fig. 1. Light-absorption curves for $1.4\cdot10^{-5}$ M solutions of arsenazo III with a pH of 2.0 (1), a complex of arsenazo III with UO_2^{2+} with a pH of 1.5(2), and a complex of arsenazo III with Th in 3.5 N HCl. SF-4 spectrophotometer, 10 mm cell.

stabilities of the complexes element-reagent and element-masking complex former. At n = 50-100 and higher, the stability of the element-reagent complex considerably exceeds the stability of the complex element-masking complex former. In Table 1 are presented the stability indices for systems of arsenazo I, arsenazo II, and arsenazo III with U^{VI}, Th, and a number of complex formers. The higher values of the stability index obtained for systems containing arsenazo III indicate the considerable stability of complexes of UO_2 and Th with this reagent.

Properties of arsenazo III. Arsenazo III is a dark red, almost black, crystalline powder. It is stable for an indefinite length of time, both as the dry solid and in solution. The color of a solution of the reagent in weak acids is rose, while in concentrated H_2SO_4 it is green, and in basic solution it is blue.

Light absorption curves for arsenazo III and its complexes with uranium and thorium are shown in Figure 1. The sharp shift of the curves (deepening of the color) upon formation of a complex together with the extremely high stability of the complexes are a favorable indication of the increase in sensitivity of the reaction. Thus, the sensitivity of the determination of uranium and thorium is 0.01-0.02 γ/ml. The optimum λ for the determination of uranium is 655 mμ, while that for thorium is 660-690 mμ (the ratio Th: reagent and the pH of the solution have an effect on the optimum wavelength). The color of arsenazo III in bases and in concentrated H_2SO_4 and the change in color upon formation of a complex with an element are in accordance with present views [9]. The color of arsenazo III in acid solutions is unexpected. Thus, it is well known that bisdiazo derivatives of chromotropic acid have deeper colors, blue and violet, as a result of conjugation of both parts of the molecule. It seems to us that the following is a satisfactory explanation of the rose color of arsenazo III: the arsono group, which is located ortho to the azo group, creates considerable steric hindrance, owing to which a planar structure of the molecule is impossible. The absence of coplanarity leads to a color for the bisdiazo compound which is not too different from the color of the monoazo compound. The steric hindrance created by the arsono also makes the synthesis of arsenazo III considerably more difficult if the synthesis is carried out by the route usually used for the synthesis of bisdiazo derivatives of chromotropic acid. We now present examples (schemes) for the determination of thorium and uranium.

Determination of thorium. The maximum color development of the Th - arsenazo III complex is observed in 4-10 N HCl. This exceeds by far the optimum acidity for the interaction of thorium with arsenazo I or arsenazo II (Figure 2). The reaction is selective; of the elements usually associated with thorium, only Zr and Ti interfere. But their effect can be sharply reduced by the introduction of oxalic acid into the solution. This was found to eliminate completely the effect of 30-50-fold amounts of Zr and 2-5-fold amounts of Ti. The very small masking of thorium itself is taken into account by the introduction of a correction. For a 25 ml volume, the recommended amounts of reagents are: arsenazo III, 0.2-0.4 mg; concentrated HCl (~ 11.5 N), 8 ml; $H_2C_2O_4\cdot2H_2O$, 400-700 mg;

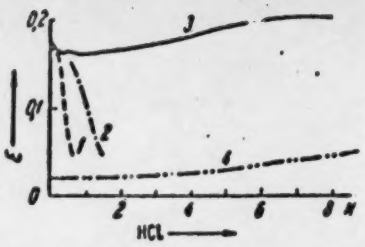


Fig. 2. Effect of pH on the development of color of complexes of thorium with the reagents: 1) arsenazo I, thorium concentration $1.2 \cdot 10^{-5}$ M, λ 650 mμ; 2) arsenazo II, thorium concentration $1.2 \cdot 10^{-5}$ M, λ 600 mμ 3) arsenazo III, thorium concentration $0.4 \cdot 10^{-5}$ M, λ 665 mμ; 4) Solution of pure arsenazo III. Concentration of reagents, $0.5 \cdot 10^{-4}$ M; SF-4 spectrophotometer; 10-mm cell.

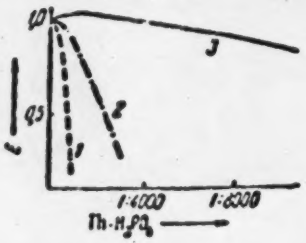


Fig. 3. Effect of phosphates on the determination of thorium with arsenazo I (1), arsenazo II (2), and arsenazo III (3). Optimum conditions.

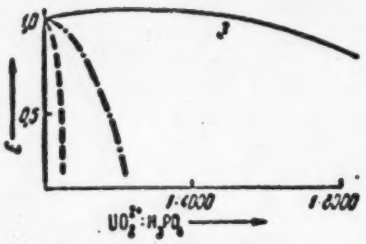


Fig. 4. Effect of phosphates on the determination of uranium with arsenazo I (1), arsenazo II (2), and arsenazo III (3). Optimum conditions.

and Th, 5-50 γ. The determination is carried out at a wave length of 665 mμ. Sulfates and 3000-5000-fold amounts of phosphates do not interfere with the determination (Figure 3).

Determination of uranium. The maximum development of color by the UO_2^{2+} -arsenazo III complex is observed at a pH of 1.7-2.5. However, a pH of 3.0 is more satisfactory for the determination of uranium in the presence of complex formers (for example, phosphates), for the effect of the impurities is less at this pH. The permissable ratio UO_2^{2+} : H_3PO_4 is 1:4000 to 1:6000 (Figure 4). The required pH of 3.0 is satisfactorily maintained by the use of a buffer mixture of monochloroacetic acid and its salts. The determination of U^{VI} must be preceded by the most complete separation possible of Th, Zr, V, Al, Cr, and the rare earths, all of which interfere. Aluminum does not affect the determination of uranium in 0.05 N HCl or in the presence of sulfosalicylic acid.

The selectivity may be sharply increased by a preliminary reduction of the uranium to the tetravalent state. The determination of U^{VI} may conveniently be carried out in 5-6 N HCl in the presence of oxalic acid, which serves to tie up the Zr, Hf, and Ti.

Elements other than Th have no effect.

Synthesis of arsenazo III. Arsenazo III can be prepared by diazonium coupling of o-aminobenzenearsonic acid with chromotropic acid. Coupling leading to the monoazo compound proceeds readily even in weakly basic medium, while an increase in the basicity to 15-25% by means of KOH is required for the preparation of the bisdiazo compound (arsenazo III). But even in this case, the yield is low. We increased the reactivities of the substances by means of the formation of chelate complexes with metals [10]. Calcium was used for this purpose, and was introduced in the form of the oxide. This immediately created the pH required for the reaction.

1.7 g (0.0078 mole) of O-aminobenzenearsonic acid was dissolved in 20 ml of water and 2.5 ml of concentrated HCl. The solution was cooled, and was diazotized by adding 1.6-1.7 ml of a 5 M solution of $NaNO_2$. The diazo solution was slowly, and with thorough stirring, introduced into a cooled solution of 1.0 g (0.0031 mole) of chromotropic acid and 2.0 g of CaO in 20 ml of water. It was allowed to stand until night or until the following day. The calcium was separated by precipitating it as the hydroxide by the addition of NaOH. The filtrate was made acid to Congo indicator, and the precipitated arsenazo III was filtered. The crude product was recrystallized 3-4 times by dissolving it in water and again precipitating it by the addition of NaCl. The yield approached stoichiometric.

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ISOMERIZATION OF C_{15}–C_{18} NORMAL PARAFFINIC HYDROCARBONS OVER SULFIDE CATALYSTS

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There have been many investigations of technological processes for the isomerization of lower n-paraffins, C_6H_{14}, C_8H_{12}, and C_6H_{16}.

For a number of years the authors have investigated the isomerization of higher hydrocarbons from kerosene and diesel fuel fractions, C_{15}-C_{18} hydrocarbons; this reaction is of considerable interest, since isoparaffins have low freezing points, -40 to -60°. Several brief reports [1,2,3] devoted to this question have appeared over the past several years. The study of the isomerization of high-molecular-weight paraffins is complicated by the occurrence of considerable cracking and other side reactions. The authors of the present article have found catalysts and conditions which make possible isomerization with good yields and with practically no cracking.

EXPERIMENTAL PART

The isomerization of C_{15}-C_{18} n-paraffins was studied at a pressure of 20 atm in a flow system. The mixture of n-paraffins and hydrogen, which was fed at a predetermined rate, was heated to 160-180° in a feed preheater, and was then fed to the reactor, which contained 250 ml of ground catalyst (particle size 1-3 mm). The reaction products passed through a condenser and then to a high-pressure receiver, from which it was transferred to a low-pressure receiver at the end of the experiment, and the gases were vented to the atmosphere. The experiments were carried out with commercial catalysts, WS_2, WS_2/NIS/Al_2O_3, and WS_2/silica-alumina. Conversions (mainly cracking) of various hydrocarbons over these catalysts have been studied, chiefly with respect to conditions for destructive hydrogenation at high pressures [4,5], but there have been only general indications of the possibility of isomerizing high-molecular weight paraffins at low pressures [6]. A fraction of n-paraffinic hydrocarbons having the composition C_{15}-C_{18} served as the feed for our experiments; this fraction had the following properties:

Boiling range, °C at 760 mm Hg	d_4^{20}	n_D^{20}	Mol. wt.	F.p., °C
272–324	0.7792	1.4377	236	+ 18

3% benzene was added to the feed as a cracking inhibitor. The inhibiting effect of benzene (in amounts not exceeding 3%) on the cracking reaction was established previously by the present authors during the isomerization of C_{12}-C_{16} n-paraffins in an autoclave in the presence of WS_2. The essential results of the present experiments are presented in Tables 1 and 2. The optimum reaction temperature (380–400°) and feed rate (1.5 liters/liter-hour) were determined for WS_2 catalyst. Under these conditions and with a mole ratio of hydrogen to paraffin of 7.5, the catalyzate contained 30% isoparaffins, 26% unconverted n-paraffins, and 44% cracking products consisting of the catalyzate fraction boiling up to 240°. With an increase in the mole ratio of hydrogen to paraffins from 7.5 to 15.8, the isoparaffin content of the catalyzate increased to 35%, and the yield of cracking products dropped to 30%. A further increase in the mole ratio of hydrogen to paraffins to 22 inhibited both the cracking reaction and isomerization, as is indicated by the freezing-point range of the isomers and the decrease in their yield (Tables 1 and 2 and Figure 1).

TABLE 1

Isomerization of C_{16} – C_{18} n-Paraffins in the Presence of Sulfide Catalysts at 20 Atm Pressure

Expt. No.	Catalyst	Temp., deg C	Space rate, liters/ /hour	Mole ratio H_2/ /paraffin	Liquid yield, wt. %	Catalyzate composition, wt.%		
						cracking products (fraction to 240°)	unconverted n-paraffins	Isoparaffins*
1	WS_2	380	1,45	7,5	85,8	44	26,4	29,5
2	Same	390	1,54	8,6	80,0	39,7	30,7	29,5
3	Same	380	1,45	15,8	91,0	30,0	35,4	35,6
4	Same	390	1,64	22	88,0	11,0	65,8	23,2
5	WS_2 — NiS — Al_2O_3	384	1,50	9	94,0	12,4	56,8	30,8
6	Same	385	1,49	12,6	96,0	9,1	73,4	17,5
7	Same	400	1,55	12,4	97,0	8,2	65,1	26,7
8	Same	432	1,60	12,4	91,5	16,3	53,3	30,4
9	Same	450	1,58	11,9	95,0	23,2	41,9	34,9
10	WS_2/silica-alumina	383	1,50	8,4	84,5	42,7	48,6	8,7

* The isoparaffins were separated by 2-fold treatment with urea of the catalyzate fraction boiling above 240°.

TABLE 2

Properties of the Isoparaffins

Expt. No.	B.p., deg C at 760 mm Hg	n_D^{20}	d_4^{20}	Mol. wt.	Temp. of first crystn.	F.p., deg C
1	250–315	1,4424	0,7804	218	–43	–84
2	242–315	1,4522	0,7905	210	–41	–65
3	240–320	1,4426	0,7841	220	–42	–64
4	242–315	1,4430	0,7808	220	–31	–48
5	238–306	1,4388	0,7862	232	–51	–72
6	250–316	1,4390	0,7885	232	–47	–60
7	238–312	1,4388	0,7865	233	–45	–60
8	240–314	1,4408	0,7918	226	–47	–67
9	238–310	1,4425	0,7928	223	–45	–66
10	242–310	1,4410	0,77[illegible]	223	–36	–64

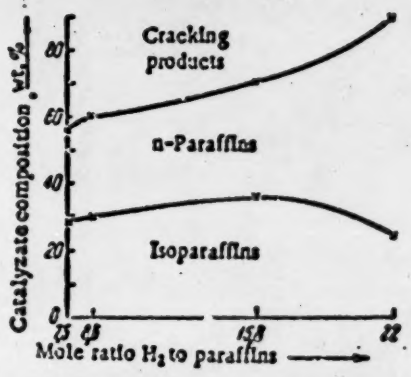

Fig. 1. Effect of mole ratio of hydrogen to paraffins on the composition of the isomerization products in the presence of WS_2.

Isomerization over the WS_2/NiS/Al_2O_3 catalyst was accompanied by considerably less cracking. Thus, under the same conditions (Experiments 5 and 2), the content of cracking products in the catalyzate was lower by a factor of 3,5 than when the WS_2 catalyst was used. Inhibition of isomerization with an increase in the mole ratio of hydrogen to paraffins was especially evident in the case of WS_2/NiS/Al_2O_3. Thus, under the conditions of Experiments 5 and 6 (385° and 1,5 liters/liter·hour), an increase in the mole ratio from 9 to 12,6 decreased the yield of isomers by almost a half while the yield of cracking products remained practically the same (12,4 and 9,1%, respectively).

The weak cracking activity of the WS_2/NiS/Al_2O_3 catalyst permits the isomerization reaction to be carried out with good yields at higher temperatures. An increase in the reaction temperature from 385 to 450° under otherwise equal conditions (Experiments 6 and 9) led to an increase in the yield of isoparaffins by a factor of 2 (Figure 2), while the amount of cracking products increased significantly only at temperatures above 430°. However, at equal isoparaffin yields, the amount of cracking products was significantly lower than in the case of WS_2.

TABLE 3

Physicochemical Properties of Narrow Fractions Separated from the Isoparaffin Mixtures from Experiments 1 and 4

B.p., deg C at 7 mm Hg	n_D^{20}	d_4^{20}	Mol. wt.	I. r. data*	
				No. of CH_2 groups	No. of CH_3 groups in side chain
Isoparaffins from Experiment 1					
117–126	1.4420	0.7845	212	9	2
129–134	1.4405	0.7833	216	11	1
139–144	1.4427	0.7860	224	9.5	2
144–147	1.4418	0.7858	226	11.5	1
143–150	1.4435	0.7887	238	14	1
Isoparaffins from Experiment 4					
131–135	1.4408	0.7833	207	12	1
138–143	1.4405	0.7860	222	12	1
143–147	1.4430	0.7860	238	12	1.5
147–150	1.4458	0.7913	235	12.5	1
150–155	1.4460	0.7923	227	13	1

* The infrared investigations were carried out by the method described in reference [7].

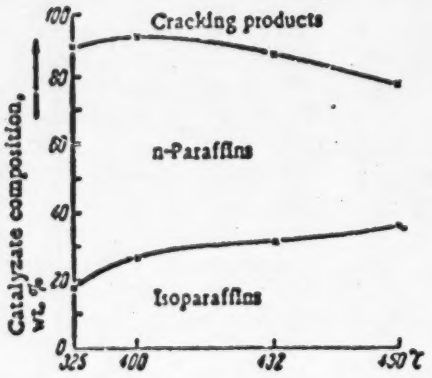

Fig. 2. Effect of reaction temperature on the composition of the isomerization products in the presence of $WS_2/NiS/Al_2O_3$.

Over WS_2/silica-alumina catalyst at 338°, a space rate of 1.5 liters/liter·hour, and a mole ratio of hydrogen to paraffins of 8.4, only 8.7% isoparaffins was obtained, while the amount of cracking products was 42.7%. Thus, this catalyst developed only a slight activity for isomerization, while its cracking activity predominated.

Isomerization over the different sulfide catalysts occurs with the formation of isomers with the same degree of branching as may be seen from the freezing point limits of the isomers. The isoparaffins from Experiments 1 and 4, obtained at different mole ratios of hydrogen to paraffins, were distilled in a column with an efficiency of 25 theoretical plates into a number of narrow fractions, which were characterized by infrared spectroscopy (Table 3).

It may be seen from the data in Table 3 that isomerization over sulfide catalysts proceeds with the formation of mono- and dimethyl-substituted isomers, and when the isomerization reaction is inhibited by high mole ratios of hydrogen to paraffins (Experiment 4), chiefly monomethyl-substituted isomers are formed.

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